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## THE RELATIVE IMPORTANCE OF THE SEVERAL FACES OF A CRYSTAL

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### ABSTRACT

A number of rules have been proposed to correlate the relative importance of the several faces of a crystal with the geometrical features of the crystal lattice. Chief of these are the rule of simplest indices, Bravais' rule, and Donnay-Harker's rule. The latter has had considerable success in formulating the relative importance of the faces of a crystal, but it is completely empirical, as are all the other rules. This paper suggests a rational basis for the rule. It is shown that if the crystal grows by the accretion of molecular chunks which are equivalent by an operation with a translation component, then Bravais' rule can be derived from crude surface energy considerations. These considerations also explain the stability of crystal faces and predict that crystals should form without faces when they grow from media of equal surface tension. The same theory accounts for the known deviations from Bravais' rule by ionic crystals.

### INTRODUCTION

The faces displayed by a crystal represent a boundary between the crystal and the medium which deposited the crystal. Thus it should be obvious that the character of the collection of faces displayed by a crystal is determined by both the crystal and the depositing medium, or, more generally, by the crystal and its environment.

There is plenty of experimental evidence that the relative sizes of the several faces of a crystal can be influenced by the environment depositing the crystal. Buckley<sup>1</sup> and Bunn<sup>2</sup> have been active in this field and have provided rival structural explanations for the mechanism of the influence of impurities in the depositing solution on the variation of crystal habit. It is also known that temperature, pressure, and rapidity of growth (i.e., other aspects of the general environment of growth) produce variations in crystal habit. While the nature of the external influences other

<sup>1</sup> Buckley, Harold E., The influence of  $\text{RO}_4''$  and related ions on the crystalline form of sodium chlorate: *Zeits. Krist. (A)* **75**, 15-31 (1930).

<sup>2</sup> Bunn, C. W., Adsorption, oriented overgrowth and mixed crystal formation: *Proc. Roy. Soc.*, **141A**, 567-593 (1933).

than impurities have not been extensively discussed, it is not difficult to advance reasonable explanations for them.

It has also been recognized that the crystal itself has an influence on its habit, and, in a crude empirical way, the general characteristics of the influence are known. Yet those crystallographers interested in this aspect of morphology have been content with the empirical relation and have not attempted to give any rational explanation of it. It is the chief purpose of this paper to suggest such an explanation.

#### ATTEMPTS TO FORMULATE THE INFLUENCE OF THE CRYSTAL

Attempts to formulate the characteristics of the crystal's influence on its own form development arose early in the history of crystallography. All such attempts were empirical formulations which sought to relate the form development to some aspect of the lattice geometry (as distinct from structure or bonding).

Perhaps the crudest approximation is the rule that faces with simplest indices are the best developed and that the importance of the faces decreases with increasing complexity of the indices. This approximation dates from Haüy's time<sup>3</sup> and has even been called the "Law of Haüy." There are other formulations which are essentially equivalent to this rule. Thus, Barker's *Principle of Simplest Indices*<sup>4</sup> provides that the important faces of a crystal can be assigned simple indices, and this implies, in turn, that importance in development of a face is related to the simplicity of the indices. Again, Goldschmidt's Law of Complication,<sup>5</sup> which recently achieved some popularity in America,<sup>6</sup> implies this relation.<sup>7</sup> The simplest-indices rule has obvious shortcomings. For example, it requires all isometric crystals to have identical form development, and it requires *all* crystals to have form developments which are related to one another by homogeneous deformations, which is obviously contrary to observation.

A much better approximation was discovered by Bravais.<sup>8</sup> Bravais' rule states that the relative importance (implying both frequency of occurrence and area) of the development of the faces of a crystal is in the

<sup>3</sup> Haüy, René Just, *Cristallographie*, 2nd ed., vol. 2, p. 155.

<sup>4</sup> Barker, T. V., *Systematic Crystallography* (Thomas Murby & Co., London 1930) p. 2 *et seq.*

<sup>5</sup> Goldschmidt, V., Über Entwicklung der Krystallformen: *Zeits. Krist.*, **28**, 1-35 and 414-451 (1897).

<sup>6</sup> Peacock, M. A., Calaverite and the law of complication: *Am. Mineral.*, **17**, 317-337 (1932).

<sup>7</sup> Buerger, M. J., The law of complication: *Am. Mineral.*, **21**, 702-714 (1936).

<sup>8</sup> Bravais, M. A., Études cristallographiques: *Jour. de l'École Polytechnique*, 167 (1851).



same order as their reticular density (or, what is the equivalent, in the same order as their interplanar spacing).

An alternative form of Bravais' rule is attributed to Fedorov. This is that the habit of a crystal is approximately that of the shape of a cell of its polar (reciprocal) lattice. This can be easily shown to follow directly from Bravais' rule, but it is less comprehensive in that it merely gives the order of development of the three important pinacoidal enclosing forms.

As Bravais' rule came into vogue in America, Goldschmidt's "Law of Complication" waned. The protagonists of Bravais' rule enthusiastically proclaimed it "The Law of Bravais" and gave the impression that it was a law of nature on the same plane as one of the laws of thermodynamics. This generality of the "law" was supported by analyses of the form developments of certain individual crystals favorable to the rule.

That the "Law" of Bravais was not quite as perfect as its proponents claimed was suspected as the numerous exceptional crystals turned up. A much better approximation was then discovered which explained many of the exceptions. This was announced as a new "law" of nature by Donnay and Harker,<sup>9</sup> who pointed out that many more crystals came into conformity with the requirements of Bravais' rule if "interplanar spacings" are interpreted to mean not only the spacings of the lattice but also to include modifications of spacings as required by those space group operations which contain translation components. This required a recognition of the same extinction conditions that occur in x-ray diffraction by crystals.

It might be pointed out here that an interesting relation exists between form development, as required by the Bravais-Donnay-Harker rule, and the powder photograph of the crystal. The order of importance of the crystal faces is exactly that of the order of appearance of the corresponding lines on the powder photograph (proceeding from  $\theta=0$  to  $\theta=90^\circ$ ), provided that no orders of a line other than the first are considered. This proviso merely takes account of the fact that one form is represented by one line, since orders of a face have no meaning.

It is important to recognize that the Bravais-Donnay-Harker rule is strictly empirical and represents an attempt to find something about the crystal which is related to the comparative development of crystal faces. It is undesirable to accept the rule as a "law," particularly in view of the embarrassing history of the designation "law" in connection with crystal form development. As a generalization it rests on the sum total of the individual cases investigated, and among these there are some serious

<sup>9</sup> Donnay, J. D. H., and Harker, David. A new law of crystal morphology extending the Law of Bravais: *Am. Mineral.*, **22**, 446-447 (1937).

exceptions.<sup>10,11</sup> Furthermore, in the cases which support the rule, there is not necessarily complete agreement between the relative reticular density sequence and the order-of-importance sequence. Nevertheless, it must be recognized that there is a strong tendency for many crystals to conform in at least a general way to the requirements of the rule. What is the explanation of the agreement?

#### PINACOID DEVELOPMENT FOR A SIMPLE CRYSTAL

To get a preliminary picture of the possible significance of the Bravais rule, consider the growth of a simple crystal. The crystal is assumed to be simple in that,

- (1) the crystal is triclinic,
- (2) the crystal is built up of discrete molecules, and
- (3) there is one molecule per unit cell.

The growth process consists of the locating of one molecule at each point of the triclinic lattice. For further simplification, suppose that the molecule has the shape of the parallelepiped unit cell. Growth then consists of the addition of blocks to the solid structure.

No assumptions are made about the specific character of the bonding between molecules in the crystal other than that ionic bonding is temporarily excluded (for reasons which will develop subsequently) and that the latent bond strength density is, on the average, uniformly distributed about the surface of the molecule. When a molecule lands on the crystal surface so as to continue the crystal structure, then the energy of the bond between molecule and crystal is (to first approximation) proportional to the area of the surface joining the molecule to the crystal. If several sites on the crystal are available to molecules, the preferred site (neglecting differential thermal effects) is the one with maximum bond strength. With the simplifying assumptions of this section, this is the site which offers the greatest area of attachment between crystal and molecule.

Consider, first, the growth process of three pinacoids, which represent, in simplified form, a series of three planes of different reticular density. Except when a new layer starts, the general conditions of the three pinacoids is shown in Fig. 1. New molecules add themselves to each layer by falling into a corner of the step on the growing surface. The corner on each of these pinacoids exposes an identical area to a molecule about to take its place in a corner. This area is the sum of the areas of the three

<sup>10</sup> Donnay, J. D. H., Tunell, G., and Barth, T. F. W., Various modes of attack in crystallographic investigations: *Am. Mineral.*, **19**, 456-458 (1934).

<sup>11</sup> Donnay, J. D. H., and Harker, David, A new law of crystal morphology extending the law of Bravais: *Am. Mineral.*, **22**, 463-465 (1937).



pinacoidal bases of the unit cell and is a measure of the first coordination of the molecule arriving at the surface. It is easily demonstrated that a molecule landing on any growing rational plane whatever (provided, as above, that the molecule is not starting a new layer) lands in a corner of the same character and achieves a first coordination measured by the area of the same three pinacoidal bases of the cell. This can be generalized for molecules of more general shape than that of a unit cell parallelepiped,

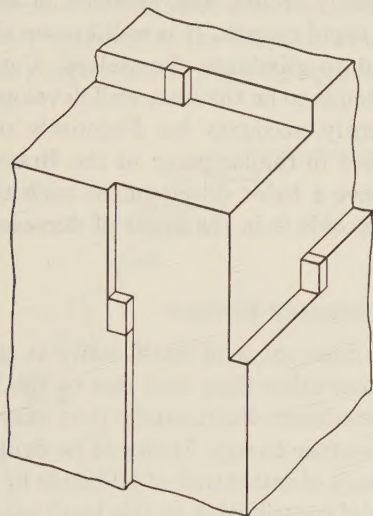


FIG. 1

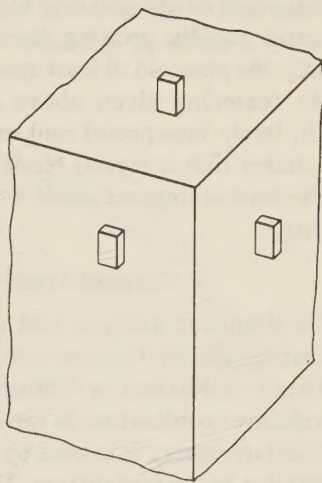


FIG. 2

with the result that it can be said that any molecule landing on a rational plane in such a way as to continue the general growth of that growing plane, does so in such a way as to achieve a first coordination measured by half the external surface of the molecule. Thus, in the growth of any rational plane, there is no differential in the immediate coordination of the system crystal-molecule and therefore, from the point of view of the energy realized by the coordination of the molecule and the plane, no plane of the crystal has an advantage over any other. Therefore if molecules rain evenly on all surfaces of a crystal, equal volumes might be expected to be added to each pinacoid (or other plane) in a given time, and consequently the planes might be expected to advance at an even rate.

But consider the situation as a layer starts: Fig. 2 shows a molecule in place on each of the three pinacoids of the simple crystal. It is evident that the surfaces of attachment are the pinacoidal bases of the cell taken one at a time. Since the volume of the cell is any base times its corresponding interplanar spacing, the area of any base is inversely propor-

tional to its spacing. Thus the surfaces of attachment of the first molecules are in the inverse order of the interplanar spacings of the pinacoids to which they attach themselves. The most likely attachment of the three possible ones is that which has the greatest coordination of attachment, namely the molecule which rests on the pinacoid of *least* interplanar spacing. It might thus be expected that the probability of starting a new layer is highest for the pinacoid of least spacing. Since the bottleneck of starting a new layer continually recurs, the pinacoid of least spacing must be the pinacoid of most rapid growth. It is well known that the most rapidly growing faces tend to eliminate themselves. Consequently the pinacoid of least spacing tends to be the least well developed.

The reasoning given above evidently accounts for Fedorov's rule, which, freely interpreted and expressed in the language of the Bravais' rule, states that a crystal tends to have a habit development such that the decreasing importance of the pinacoids is in the order of decreasing spacing.

#### COORDINATION AND SURFACE ENERGY

The simplified analysis just given does not lend itself easily to generalization, chiefly because coordination other than that due to the immediate coordination is difficult to evaluate. Fortunately it is easy to reformulate coordination in terms of surface energy. It should be evident that surface energy is caused by the lack of saturation of all bonds in the crystal due to the free surface. The chief contribution to this bond energy comes from bonds at the surface, and thus from surface coordination, but secondary coordinations are also involved. Thus, surface energy and total realized coordination energy across the free surface are complementary.

Returning, now, to the simple case discussed in the last section, the situation can be summarized as follows: If several sites are available to a molecule, the preferred site is that which permits the molecule to attain the greatest immediate coordination. Evidently this statement ought to be corrected so that its last part reads, "which permits the molecule to attain the greatest total coordination." In view of the complementary nature of realized coordination and surface energy, this can also be stated in the following terms: If several sites are available to a molecule, the preferred site is the one for which the molecule achieves the greatest decrease in its surface energy. Furthermore, growth is least rapid for the plane which requires, for the starting of each new layer, the attachment of a molecule in the position which leads the molecule to retain the most surface energy (which is the complementary way of saying that the molecule achieves the least total coordination or least bonding energy).



## SURFACE ENERGY AND BRAVAIS' RULE

Bravais' rule is usually stated in such a way as to involve the "importance" of the development of a face. An equivalent, but somewhat more convenient form of the rule for the present requirements is that the faces of a crystal have growth velocities in the inverse order of their interplanar spacings. If this is true, and if the analysis of the last section is also true, this implies that the residual surface energies of the attached molecules which start new layers are in the inverse order of the interplanar spacings of the faces to which they are attached. That this is at least roughly correct can be appreciated from Fig. 3, where a crystal

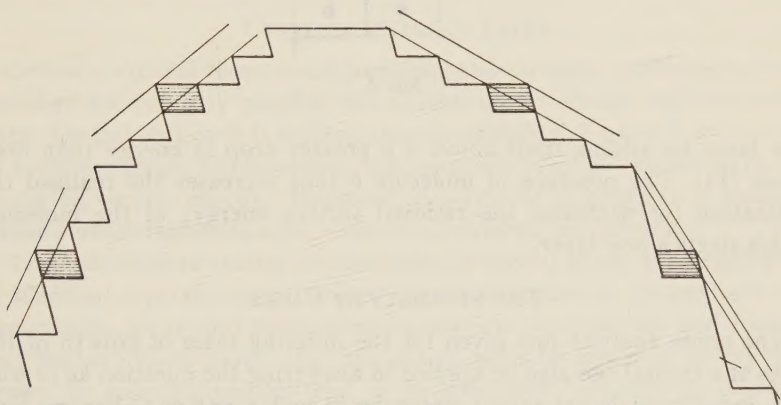


FIG. 3

represented as being made up of parallelepiped cells. (If ellipsoids are substituted for these parallelepipeds, the following feature still holds.) It will be observed that the molecules shown shaded, which start the new layers, project above the general levels of the planes by an amount equal to the interplanar spacing,  $d_{hkl}$ . When a molecule starts a new layer, it thus constitutes an excrescence on the layer, the height of which is roughly a measure of the residual surface energy of the molecule which starts the new layer.

This analysis is quite crude, but it appears to be essentially correct for the simple case taken for study. In this case, the Bravais' rule appears to operate because the residual surface energy of the added molecule is a function of the way the molecule fits into the surface, and this, in turn, is a function of  $d_{hkl}$ .

That this crude analysis is essentially correct can be appreciated by considering the contours of potential in the neighborhood of a location on

a simple crystal surface. In Fig. 4, the full line  $AB$  may be taken to represent a contour in the energy field of a plane with indices (11). At  $B$ , the main contribution comes from molecule  $a$ . For a plane of index (12), a molecule  $b$  is also part of the surface, and it also contributes a potential at  $B$  of a magnitude comparable with that contributed by molecule  $a$ . For this second plane, therefore, point  $B$  has a greater energy than it had for the first plane. Plane (12), therefore, offers a molecule which starts a

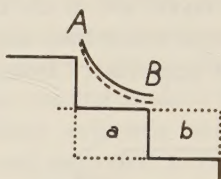


FIG. 4

new layer by adding itself above  $a$  a greater drop in energy than does plane (11). The presence of molecule  $b$  thus increases the realized coordination (or decreases the residual surface energy) of the molecule which starts a new layer.

#### THE STABILITY OF FACES

The crude analysis just given for the differing rates of growth of the faces of a crystal can also be applied in answering the question as to why high-index faces do not accept molecules in such a way as to become low-index faces. For example, Fig. 5 shows a surface with intercepts 1, 3.

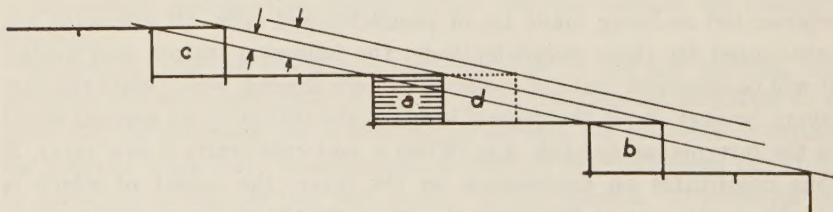


FIG. 5

When the plane grows, molecule  $a$  is first added to the surface, temporarily changing the slope of that region of the surface to intercepts 1, 2. Why does not another molecule,  $d$ , then add itself to the surface next to  $a$ , thus changing the intercepts of the surface to 1, 1, and so on, until the crystal consists of pinacoids only? It will be observed, however, that if both molecules  $a$  and  $d$  are added to the surface, the surface ex-



crecence due to  $a$  plus  $d$  is twice as high as that due to  $a$  alone, and hence molecules added to the surface after  $a$  arrives preferably attach themselves at neighboring positions similar to  $a$ , such as  $b$  and  $c$ . Thus, a plane rejects molecules which attempt to add themselves in positions which would change the index of the plane to one of less complexity.

A very similar analysis shows that a plane rejects molecules which attempt to add themselves in positions which would change the index of the plane to one of greater complexity. Thus a plane tends to avoid variations in its slope because of surface energy barriers. In this way a crystal plane, once started, is stable, and maintains its slope, and therefore its identity.

### CRYSTALS WITHOUT FACES

Crystals without faces would be anomalous to some crystallographers, yet they are not only possible but normal under certain circumstances. From the last section it is evident that the stability of a face is a function of surface energy. Furthermore, the very existence of crystal faces depends on surface energy. Therefore, if a crystal is grown in a medium whose surface tension is equal to its own, no faces can develop.

This condition is exactly realized when a crystal grows in an aggregate of identical crystals, as in the case of recrystallization. Under such circumstances, no crystal form development is to be expected, and Harker and Parker<sup>12</sup> have shown that the shapes actually assumed by crystals grown by recrystallization tend to be polyhedra bounded by dihedral angles of  $120^\circ$  whose orientations are independent of any vectorial properties of the crystal.

The condition is nearly realized when a close-packed crystal forms from a melt of the pure metal. In this case, the melt is nearly close-packed, and the forces on an atom at a metal-melt interface are nearly alike on both sides, thus causing the interfacial tension to nearly vanish. For this reason, copper crystals and zinc crystals formed from pure melts have typically rounded forms. On the other hand, when a metal crystal and its melt differ considerably in density, as in the case of bismuth, then the interfacial tension between crystal and melt is considerable. Under these circumstances crystals with well-developed faces form from a pure melt.

### THE DONNAY-HARKER RULE

In the development given above, it was assumed that the crystal was characterized by molecules which were translationally equivalent. The

<sup>12</sup> Harker, David, and Parker, Earl R., Grain shape and grain growth: *Trans. Amer. Soc. Met.*, **34**, 156-195 (1945).

residual surface energy of the molecule was due to the projection of this molecule above the general level of the nearly smooth surface. It is evident that the same general state of affairs will hold if the molecules are equivalent by other operations having a translation component, namely screw axes and glide planes. Under such circumstances, some planes related by the translation-bearing operation (for example, in symmetry  $Pc$ , planes  $(h0l)$  with  $l$  odd) have submultiple spacings, and therefore have lower excrescences when molecules add themselves to the surfaces. Consequently the surface energy conditions of molecules added to these planes are equivalent to those of planes with corresponding submultiple spacings. These planes tend to eliminate themselves by rapid growth as compared with other planes. Thus the Donnay-Harker rule also follows from surface energy considerations.

#### DEVIATIONS FROM THE BRAVAIS-DONNAY-HARKER RULE

Notable deviations from the generalized Bravais rule have been found. These include certain individual nonconforming planes<sup>13</sup> in certain crystals and also crystals which do not conform at all. Such exceptions should be a warning that the effect is not referred to the appropriate variable. Specifically, it suggests that the variable in the crystal's effect on its own habit is not as simple as interplanar spacings based on either planes rational with respect to lattice translations or rational with respect to translation-bearing symmetry operations in general. A general explanation of certain deviations from Bravais' rule is therefore that the planes of growth need not always be rational. When this is the case, there is no need for the habit of a crystal to conform with Bravais' rule.

In the following sections, some of the causes of deviation from Bravais' rule are discussed.

*Deviations Due to Growth from Ionic Solution.*—Among the crystals which do not conform to the Bravais' rule at all are the class of crystals which are notably ionic. Since the ionic crystals which have been studied for conformity with the rule have been grown from solutions which ionize the solute, it is evident that molecules cannot possibly be deposited on the surface of the crystal from such solutions. Rather the solutions must deposit particles which are of two kinds, namely the two oppositely charged ions, and these are not equivalent by any symmetry operation of the crystal. For this reason the excrescences on the surface of the crystal caused by adding the particle to the surface, as the plane grows, is smaller

<sup>13</sup> For example, see: Taylor, E. D., The morphology of columbite crystals: *Am. Mineral.* **25**, esp. p. 134 (1940); also Nuffield, E. W., and Peacock, M. A., Studies of mineral sulphosalts: VIII, *Univ. of Toronto Studies*, Geol. Ser., No. **49**, 33 (1945).



than it would be if the entire motif were added. It is thus no longer possible to measure the size of the projection by  $d_{hkl}$ , and consequently the crystal does not conform to Bravais' rule.

As outlined above, the Bravais rule works because the crystal builds up by the addition of translationally equivalent units, and this requires that the new layers added are always rational lattice planes. When the entire motif is not deposited as a unit, then the crystal cannot be built up by the addition of layers which are rational planes, for some layers must be interleaved between rational layers. Such interleaved layers can be fictitiously described as rational provided a fictitious translation-bearing operation is assumed between them. This fictitious operation also brings some positive and negative ions into coincidence with one another. Therefore, if a subcell is chosen from the lattice which is composed of such fictitious translations (three which bring positive and negative ions into coincidence) the crystal comes into fictitious conformity with Bravais' rule.

*Deviations Due to Growth by Accretion of Molecules Which Are Not Crystallographically Equivalent.*—In discussing the rational basis for Bravais' rule with Dr. J. D. H. Donnay about four years ago, the writer pointed out that the form development of superstructures ought to follow that required by Bravais' rule for the basic structure rather than that required for the superstructure itself. Dr. Donnay tested this prediction by studying the form development of orthorhombic low-chalcocite, which was known to the writer to be related as a superstructure to hexagonal high-chalcocite.<sup>14</sup> In a private communication to the writer, Dr. Donnay reported that the morphology of high-chalcocite did indeed follow that of the simpler structure upon which it is based.

This general behavior is to be expected on the basis of the theory of form development presented in this paper. Suppose, for example, that a crystal is composed of two kinds of chemically equivalent molecules which are located in the crystal in non-equivalent sites. Unless a polymerization has taken place in the solution from which the crystal is grown, the growth of the faces of the crystal can be expected to take place by addition of the individual molecules to the faces. This means that motif fractions rather than translation-equivalent motifs land on the crystal faces during growth. Now Bravais' rule can be rationalized along the lines discussed in this paper only if growth is by motif units which are equivalent by an operation with a translation component, a feature which does not obtain in the case under consideration. Consequently Bravais'

<sup>14</sup> Buerger, M. J., and Buerger, N. W., Low-chalcocite and high-chalcocite: *Am. Mineral.*, **29**, 55-65 (1944).

rule cannot be expected to hold in this case. Of course the reason for this is that the surface energy due to the excrescence can be measured by  $d_{hkl}$  only if the added molecular units are translation-equivalent. When the unit added is a motif fraction, the excrescence due to the addition of the molecule is less than it would be if the entire motif were added and its height follows a different rule. Indeed it follows, at least roughly, the rule that its height is approximately that which it would be if all molecules were translation-equivalent, and this is so only if the structure is referred to the cell and symmetry of the basic structure.

In a rough way, the discussion just given applies to cases where two chemically non-identical molecules, which do not associate in solution, add themselves to the surface of a growing crystal. The crystals in these two cases correspond with *distortion structures* and *substitution structures* respectively in the theory of *derivative crystal structures*.<sup>15</sup> Provided association does not take place in the solution, crystals with derivative structures can be expected to display a form development which deviates from the Bravais-Donnay-Harker rule in the direction of the habit to be expected from the basic structure.

*Deviations Due to Molecular Asymmetry.*—In the rationalization of Bravais' rule it was assumed that the molecule was at least as symmetrical as the cell of the lattice. When this is not so, then it does not follow that the surface energy of the attached molecule is measurable simply by  $d_{hkl}$ . Thus, in the accretion of polar molecules to the surfaces of polar crystals, one should not expect the same rate of growth for all faces of identical spacing. For example, if the crystal lacks a center, one would not expect the same rate of growth for  $hkl$  and  $\bar{h}\bar{k}\bar{l}$ , in spite of the fact that  $d_{hkl}$  and  $d_{\bar{h}\bar{k}\bar{l}}$  are identical. The reason, of course, is difference in surface energy.

*Deviations Due to Non-uniform Bond Density.*—One of the simplifying assumptions which were made was that the added molecule has a uniform distribution of bond density. When this is the case, the coordination energy realized when the molecule adds itself to the crystal is a purely geometrical function of the manner of attachment of the molecule to the crystal. If, however, some aspect of the molecule's surface is characterized by a concentration of strong bonds, the preferred mode of attachment of the molecule is no longer a simple function of geometry, but is influenced by the location and strength of the strong bonds. The coordination energy realized when the molecule attaches itself is therefore no longer a simple function of  $d_{hkl}$ , and it cannot be expected that Bravais' rule will be strictly obeyed. The deviation from Bravais' rule to be expected in such

<sup>15</sup> Buerger, M. J., Derivative crystal structures: *J. Chem. Phys.*, **15**, 1-16 (1947).



cases is in the direction of the reduction of importance of faces parallel to the surface of strong bond concentration in the molecule starting a new layer, and an increase in importance of faces parallel to the surface of low bond concentration in the molecule starting the new layer.

#### VARIATION OF HABIT DUE TO IMPURITIES

It is not the function of this paper to discuss in any detail the influence of the environment on the form development of the crystal. Nevertheless it is desirable to draw attention at this point to the fact that the influence of impurities on form development can be considered from the viewpoint just adopted for considering the influence of the "normal" molecules on the habit of their crystal. If impurities are present, then both the impurity particles (which may be molecules or ions) and normal molecules may compete for positions of high coordination on the crystal surfaces. Since impurity and "normal" molecules are different, a site of high coordination for one particle is not necessarily identical with a site of high coordination for the other. Nevertheless, realized coordination energy, or its complement, surface energy, is the feature which governs the preference of sites in each case. This should be the guiding principle in seeking to predict which faces have their growths most retarded by the adsorption of impurity particles.

The influence of the impurity is more complex than that of the normal particle, however, for the impurity particle may be included as a particle in a layer being formed. Its effect on slowing down the growth of the particular face may not be felt until the next layer is about to cover the impurity in the first layer. When this occurs, it may be impossible for the second layer to continue its growth until the foreign particle has been removed by energy competition and replaced by a normal particle. A new second layer may fortuitously start elsewhere on the first layer before this can occur.

#### CONCLUSION

Those who have hitherto interested themselves in the influence of the crystal on its own form development have followed a purely empirical course and have arrived at a correlation of form development with lattice geometry. In this paper there has been an attempt to rationalize these empirical findings along lines of simple energy considerations.

Such considerations lend rational support to the Bravais' rule and its generalization. On the other hand, they throw emphasis on another aspect of crystal growth. Whereas Bravais' rule emphasizes purely the lattice geometry of the growing crystal, energy considerations make it plain that emphasis should be focussed on the characteristics of the particles which

arrive at the crystal surfaces during the growth process. When there is a simple relation between the characteristics of the arriving particles and the lattice geometry the whole growth effect can be formulated in terms of lattice geometry alone. When the arriving particles have characteristics other than mere geometrical shape to be taken into consideration, then the habit effect cannot be made functional upon lattice geometry only, and deviations can be expected from Bravais' rule.

Thus one of the most fundamental factors in determining crystal habit is the characteristics of the particles which arrive at the crystal surfaces, including both their geometry and physics of bonding. When the particle which would normally be added to the crystal to continue its structure must compete with "impurity" particles, then the corresponding characteristics of the impurity particles constitute another fundamental factor in determining habit. Both lattice geometry and bonding characteristics of the crystal constitute a third factor. Only in special cases can all three factors be formulated as a function of lattice geometry alone.



FUSED WOOD-ASH STONES: FAIRCHILDITE (n. sp.)  
 $K_2CO_3 \cdot CaCO_3$ , BUETSCHLIITE (n. sp.)  
 $3K_2CO_3 \cdot 2CaCO_3 \cdot 6H_2O$  AND CALCITE,  
 $CaCO_3$ , THEIR ESSENTIAL  
 COMPONENTS\*

CHARLES MILTON AND JOSEPH AXELROD

ABSTRACT

Stones found in the trunks of standing partly burned forest trees are produced by fusion and ensuing crystallization of the ash of the wood. Freshly formed stones consist essentially of a new mineral fairchildite, anhydrous potassium calcium carbonate,  $K_2CO_3 \cdot CaCO_3$ . On wetting, or by atmospheric hydration, this is converted to buetschliite, a second new mineral, a hydrous potassium calcium carbonate,  $3K_2CO_3 \cdot 2CaCO_3 \cdot 6H_2O$ , and calcite. On further leaching the buetschliite is decomposed to calcite with removal of the water-soluble potassium carbonate. The presence of the first three carbonates in wood-ash stones is established, and a general account of them with a review of pertinent literature is given. The artificial compounds corresponding to fairchildite and buetschliite were prepared and analyzed by Otto Buetschli in 1901-1905, but have not hitherto been reported in nature. Fairchildite is hexagonal,  $\epsilon=1.48$ ,  $\omega=1.530$ , and buetschliite is probably also hexagonal, with  $\epsilon=1.455$  and  $\omega=1.595$ .

OCCURRENCE

Stones of a peculiar type have been found within the trunks of standing partly burned trees at many localities in the forests of the western United States during the last twenty five years. These stones were obviously unlike those of the regional soil, and most of the finds gave rise to diverse conjectures as to their source. Although several investigators, as Englis and Day (1)† and Kienholz (2) had correctly described the essential nature and origin of the stones as early as 1929, few foresters appear to have been acquainted with their work, and as recently as 1938, there was a Sunday story in the *Oregon Journal* (October 2, 1938) by Louise E. Brogan, entitled "Do meteorites start fires in the forest?" (3). Moreover, correspondence in the writers' files seems to indicate that even some authorities on forestry have failed to understand the nature of these peculiar stones. It has therefore appeared desirable to assemble the recorded data, to discuss relevant studies in other fields, and to carry through such laboratory study as was necessary to make clear the natural history of wood-ash stones.

The number of localities where these stones have been obtained is fairly large, and doubtless, once the nature of the stones is generally

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† References cited in bibliography at end of paper.

known, many more occurrences will be noted. Some of the recorded occurrences with dates are:

- 1924 Clearwater National Forest, Idaho (2).
- 1925 Columbia National Forest, Washington (2), (in a score or more trees).
- 1926 Kaniksu National Forest, Idaho (2)
- 1927 Umatilla National Forest, Oregon (2), (noted in the forestry journal "Six Twenty Six" September 1927, with discussion of origin, November 1927).
- 1927 Coeur d'Alene National Forest, Idaho (2), (noted four years after fire).
- 1943 Grand Canyon National Park, Arizona (4).

Two of the occurrences listed above have been available for this study: The Kaniksu National Forest stone of the 1926 fire, and the Grand Canyon National Park stone of 1943. The chemical work on the former by Englis and Day (1) has been supplemented by microscopic and x-ray study, and the latter has been investigated chemically, optically, and by x-rays.

A letter (5) from Hugo Winkenwerder, Dean of the College of Forestry, University of Washington, states that "this stuff has been found rather often in our white fir and hemlock in this region of the country. . . ." On the other hand, there is no instance known to the writers where such stones have been found east of the Rocky Mountains. A letter addressed some years ago to the Chief of the Forest Service, Department of Agriculture, in Washington, D. C., regarding wood-ash stones, was referred to the Madison, Wisconsin, Forest Products Laboratory; but a reply from the Senior Chemist (6) of the Laboratory indicated that little if anything was known about them.

#### LITERATURE RELATING TO FUSED WOOD-ASH STONES

The first published description of these stones appears to have been in 1929, when D. T. Englis and W. N. Day, chemists at the University of Illinois, wrote a brief note in *Science* (1). Their interest was mainly in the chemical composition of the stones, or, as they termed them, clinkers. From analyses of three of these stones, and of sound wood (Analyses 1, 2, 3, and 4 of Table 2), they concluded that there was "no justification for the assumption that the clinkers were of meteoric origin" as had been supposed by some, but rather that "the peculiar rock-like character of the clinkers is probably due to the collection of a large quantity of ash in the hollow snag, followed by occasional wetting from rain and finally a fusion of the mass, during a later vigorous burning of the surrounding wood."

Later that year R. Kienholz (2) botanist at the University of Illinois, who had collected the specimens analyzed by Englis and Day, wrote a more detailed account, including many observations of especial interest.



He listed five or six occurrences, all in the forests of the western United States. The trees in which the stones were found were mostly western hemlock (*tsuga heterophylla*), also Douglas fir (*pseudotsuga taxifolia*), and, occasionally, white fir (*abies grandis*), noble fir (*abies nobilis*), and, possibly, western white pine (*pinus monticola*). The stones only formed in rotten heartwood, usually in hemlocks affected by the Indian Paint fungus (*echinodontium tinctorum*) and in Douglas firs affected by the fungus (*trametes pini*). In localities where the Indian Paint fungus was not prevalent, no clinkers were observed following forest fires. Kienholz also mentions that similar clinkers had been observed with a different origin, namely in the fireboxes of boilers burning clean hemlock sawdust. The role of the fungus therefore in the formation of these stones is not an essential one, but merely to prepare the tree for the special mode of combustion, described below, that results in these stones. Kienholz cites various observers as having found the stones in deep cylindrical pockets from 2 to 40 feet deep, and from 4 to 40 feet above the ground, and always in trees a foot or more in diameter; younger trees had apparently not been subjected long enough to the action of the fungus, in producing the rotten heartwood. The stones varied in quantity in a single tree, from one to a hundred pounds or more; and a single chunk of 16 or 18 inches in diameter was found. The length of time that a tree burned could run into weeks or months, or even through an entire winter. No clinkers ever formed in logs burning on the ground, or in trees that burned upwards from a rotten butt. All of the stones slaked visibly on exposure. Kienholz remarked that "minerals probably do not crystallize out in the formation of the clinker, as has been held, but there is a fusion of the material brought about by the high temperature." This statement is not quite correct, for there are crystalline compounds—minerals—formed in the cooling of the fused mass.

In 1938 the *Portland Oregonian* (7) printed a news item as follows: "A meteorite, still white hot, was found buried in the smoking hole of a large white fir tree near La Pine, Oregon . . . the patrolmen found smoke issuing from a hole in the tree 60 feet from the ground. . . . They felled the tree . . . and found a glowing meteorite, described as of the size of a ten quart water pail. The metallic mass, resembling smelter slag, had penetrated the wood to a depth of 14 inches and was shattered by the impact . . . ." The stone was described as of light color and of light weight, and full of holes. The account was carried by the press services, and the story appeared in the Bend, Oregon, *Bulletin*, in *Time*, and in the *Christian Science Monitor*. J. Hugh Pruett in *Popular Astronomy* (8) the following year summarized the knowledge of this occurrence.

The interest of the writers in these stones dates from 1939 when Marcus

Goldman, geologist of the Geological Survey, kindly showed one of us (C. M.) a specimen of the Kaniksu stone described by Kienholz. This interest was renewed in 1944 when H. E. Gregory, geologist of the Geological Survey, referred to the Chemical Laboratory of the Geological Survey a stone from the Grand Canyon National Park, found 56 feet up in a white fir tree previously struck by lightning. In a letter to C. S. Ross, petrologist of the Geological Survey, Professor Gregory wrote: "Although it has been determined as fused limestone there is no way of explaining the presence of so large a piece of limestone in the top of a tree. . . . I am more inclined to consider the material as fused ashes."

In a brief popular account of these wood-ash stones by C. Milton (9) are photographs of a piece of the Kaniksu stone, and microphotographs of the Grand Canyon Stone referred to the Geological Survey by Gregory. There are also photographs of the tree from which the stones were taken made by the Forest Service ranger, William J. Kennedy.

Among the erroneous ideas that have been held concerning these stones, the following may be mentioned briefly: that they are meteorites, that they are fused limestone, that they are pathological growths in the living tree, that they are produced by excessive evaporation of sap, and that they are lightning-fused ash.

#### APPEARANCE AND MICROSTRUCTURE

The two specimens studied have somewhat different aspects, the Kaniksu stone being the more homogenous, and the Grand Canyon stone being markedly heterogenous. Both contain charcoal inclusions or blackened carbonaceous areas. The appearance of the stones is shown in Fig. 1. The Kaniksu stone is dense and stony, light-grayish in color, cracked by a few spall-like fissures along which it breaks in sharply angular fragments a centimeter or two across. There is some indication of flowage of the material during fusion, and a few deep rounded holes may be ascribed to escape of gases during fusion. After twenty years the stone shows little or no sign of disintegration or alteration. The Grand Canyon specimen varies from a hard internal bluish-gray stony mass to a crumbly white porcellanic crust; it appears to be disintegrating at a very slow rate. From the observations of others, recorded in letters to the writers, it seems that the other wood-ash stones are similar to these in their general character.

The preparation of thin-sections of these stones for microscopic study is rather difficult. The more friable ones require a preliminary cementation with Canada Balsam or other hard embedding medium. Water decomposes the stones, therefore kerosene or other inert liquid must be employed in grinding the sections. Because of the hydrous character of

much of the crystalline material of the stones, they cannot be heated too much. With these precautions observed, however, fairly satisfactory thin sections can be made. The illustrations, Figs. 2, 3, 4, and 5, show the microstructure of wood-ash stones. The first impression one obtains in studying these thin sections is that of a disorderly array of a badly crys-

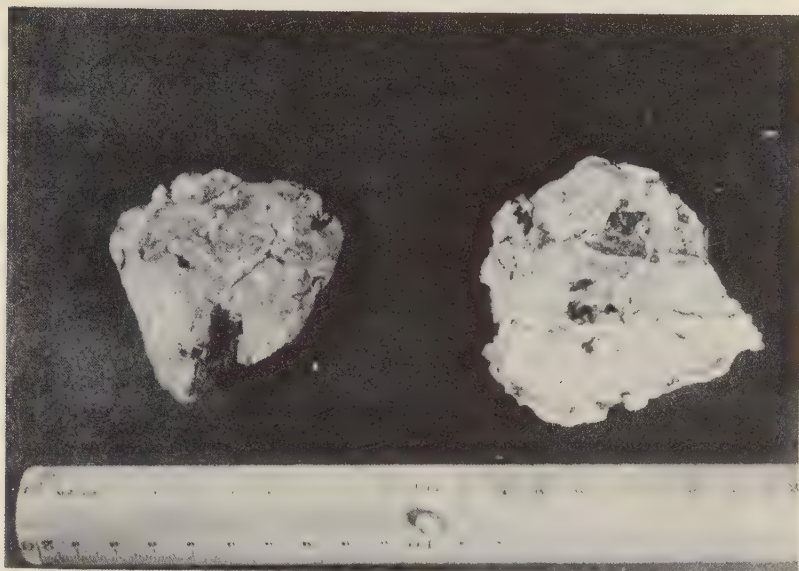


FIG. 1. *Left:* Stone from Kaniksu National Forest, Coolin, Idaho. Black embedded fragments are charcoal. *Right:* Stone from Grand Canyon National Park, Arizona. Shows striated surface caused by molding of fused ash against charcoal, which was temporarily preserved from combustion by lack of oxygen.

tallized aggregate, but this largely resolves itself on study. The most striking feature is the long blades of moderately birefringent clear colorless fairchildite,  $\text{K}_2\text{CO}_3 \cdot \text{CaCO}_3$ , showing very little relief against the Canada Balsam (Fig. 2). Most of the fairchildite however has altered to buetschliite,  $3\text{K}_2\text{CO}_3 \cdot 2\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ , which is usually difficult to distinguish in thin-section from calcite.

At places, however, the abundant calcite in these stones can be recognized by its characteristic rhombohedra, and by the "twinkle" effect (difference in relief observed on rotating the section) observable when using the lower nicol only. Much of the thin-section however remains at best difficultly decipherable, and looks like a heterogenous, carbonaceous, extremely fine grained crystalline aggregate. In fact, without the help of





FIG. 2. Fused wood-ash stone, Kaniksu National Forest, Idaho. Shows slightly altered lath-shaped cross-sections of fairchildite in a fine groundmass containing buetschliite and calcite. This thin-section shows rather more and better fairchildite than usually seen.  $\times 30$  ordinary light.

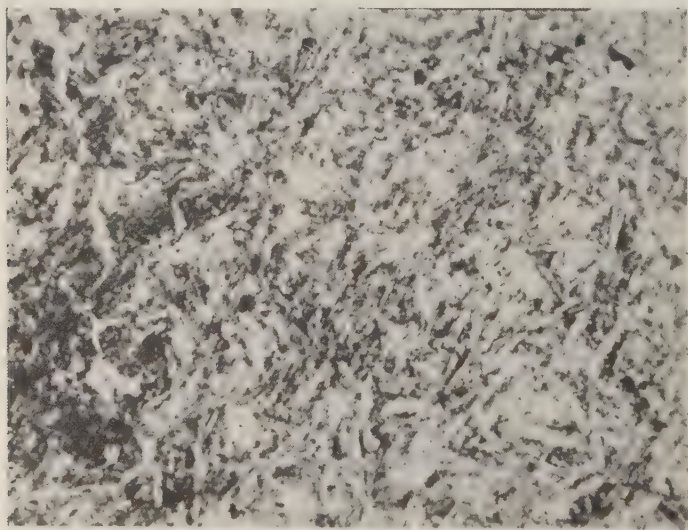


FIG. 3. Fused wood-ash stone, Grand Canyon National Park, Arizona. Shows fairchildite largely replaced by buetschliite and calcite, which retain the form of the original fairchildite.  $\times 30$  ordinary light.

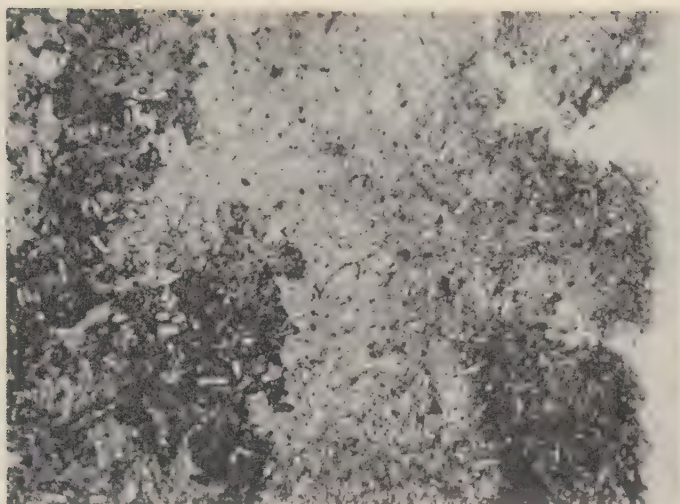


FIG. 4. Fused wood-ash stone Grand Canyon National Park, Arizona. This section was ground with water instead of oil; under these conditions decomposition of the fairchildite has produced buetschliite and calcite. The buetschliite has crystallized in characteristic stubby barrel-shaped crystals.  $\times 30$  ordinary light.



FIG. 4a same as Fig. 4 under higher magnification.  $\times 120$  ordinary light.

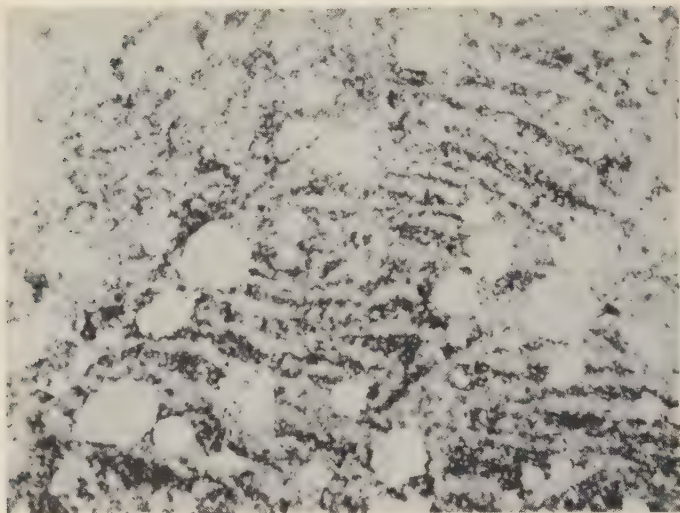


FIG. 5. Fused wood-ash stone, Grand Canyon National Park, Arizona. Shows buetschliite-calcite aggregate replacing fairchildite. The dark streaks are carbonaceous particles, segregated during crystallization of the fairchildite. The rounded clear areas are holes, caused by formation of carbon dioxide (and monoxide) from combustion of wood or charcoal during fusion of the ash; or, perhaps, by formation of carbon dioxide produced in the thermal decomposition of fairchildite at very high temperatures.  $\times 30$  ordinary light.

$\alpha$ -ray study, the interpretation of the petrographic evidence would remain a most difficult and uncertain matter.

#### X-RAY STUDY

Figure 6 shows X-ray powder patterns obtained from the various substances under consideration.

From the  $\alpha$ -ray study it appears that on wetting, or on slow hydration, in air, fairchildite ( $\text{K}_2\text{CO}_3 \cdot \text{CaCO}_3$ ) forms buetschliite ( $3\text{K}_2\text{CO}_3 \cdot 2\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ). Leaching decomposes buetschliite, leaving residue of calcite. When the natural wood-ash stones are remelted in the laboratory fairchildite forms again, insofar as the stone has not previously been leached of its potassium carbonate content; the calcite present in the remelted stone is to some extent a measure of the degree of previous leaching. Presumably therefore, wood-ash stones originally consisted of the anhydrous fairchildite, subsequently hydrated to buetschliite. As buetschliite, both the natural and the synthetic material are firm and coherent; but on leaching, with formation of calcite, the synthetic material crumbles to powder and the natural mineral probably does also. As long as the wood-ash stones retain their stony character they contain con-



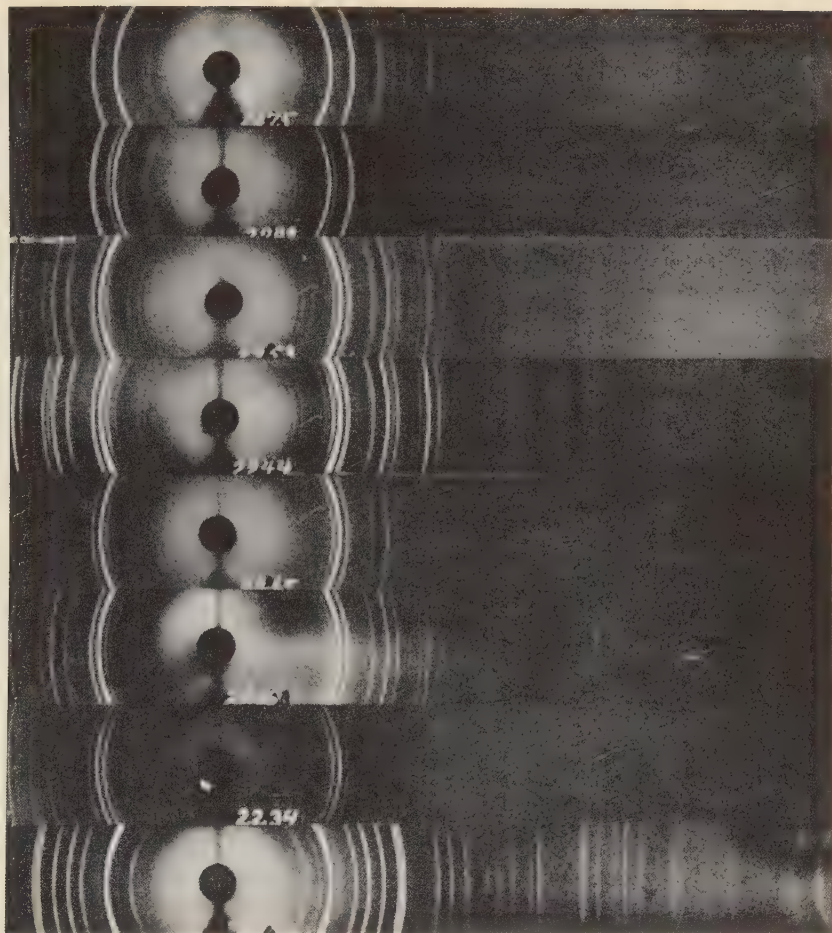


FIG. 6-A. Synthetic fairchildite made by fusion of components (film 2275). 6-B. Re-melted (in laboratory) stone from Grand Canyon National Park, Arizona. It is a mixture of fairchildite and calcite, with an unidentified substance, and a little buetschliite (presumably formed by atmospheric hydration from fairchildite) (film 2243). 6-C. Synthetic buetschliite prepared from oyster shell according to Buetschli's method described in the text (film 2253). 6-D. Synthetic fairchildite, after five months' exposure in the laboratory, giving the buetschliite pattern, without observable calcite lines (film 2244). 6-E. Stone from Kaniksu National Forest, Coolin, Idaho, after fifteen years' exposure in the laboratory. A hole was drilled through the outer portion, and the interior material x-rayed. The pattern is almost entirely that of buetschliite, with no observable fairchildite lines (film 2265). 6-F. Stone from the Grand Canyon National Park. A sample from the interior gives the same pattern as the Kaniksu stone (film 2266). 6-G. Wetted synthetic fairchildite. Patterns from buetschliite, a little calcite, and undecomposed fairchildite are seen (film 2234). 6-H. Completely leached synthetic fairchildite; only calcite remains (film 2240).

siderable potassium carbonate in chemical combination, either as fairchildite or as buetschliite.

Measurements of the powder patterns of fairchildite (film 2275) and of buetschliite (film 2244) are given in Table 1.

TABLE 1. MEASUREMENTS OF X-RAY PATTERNS

| Fairchildite<br>$\text{K}_2\text{CO}_3 \cdot \text{CaCO}_3$ |          | Buetschliite $3\text{K}_2\text{CO}_3 \cdot 2\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ |          |          |          |          |          |
|-------------------------------------------------------------|----------|--------------------------------------------------------------------------------------|----------|----------|----------|----------|----------|
| <i>d</i>                                                    | <i>I</i> | <i>d</i>                                                                             | <i>I</i> | <i>d</i> | <i>I</i> | <i>d</i> | <i>I</i> |
| 6.64                                                        | m        | 4.97                                                                                 | vw       | 1.455    | vw       | .905     | w        |
| 4.59                                                        | w        | 4.52                                                                                 | w        | 1.420    | vw       | .896     | w        |
| 4.31                                                        | vw       | 4.15                                                                                 | vw       | 1.380    | vw       | .882     | w        |
| 3.53                                                        | vvw      | 3.25                                                                                 | w        | 1.345    | m        | .863     | vw       |
| 3.33                                                        | vw       | 3.16                                                                                 | vw       | 1.263    | m        | .853     | w        |
| 3.19                                                        | vs       | 3.03                                                                                 | s        | 1.246    | m        | .844     | vw       |
| 2.689                                                       | w        | 2.860                                                                                | vvs      | 1.230    | w        | .837     | vw       |
| 2.641                                                       | s        | 2.688                                                                                | s        | 1.217    | m        | .827     | vw       |
| 2.283                                                       | vw       | 2.306                                                                                | w        | 1.205    | vw       | .822     | vw       |
| 2.211                                                       | m        | 2.251                                                                                | ms       | 1.130    | vw       | .813     | vw       |
| 2.154                                                       | m        | 2.070                                                                                | s        | 1.118    | vw       | .790     | vw       |
| 2.027                                                       | w        | 2.012                                                                                | m        | 1.108    | vw       | .777     | vw       |
| 1.880                                                       | m        | 1.960                                                                                | ms       | 1.101    | w        | .....    |          |
| 1.749                                                       | vvw      | 1.751                                                                                | m        | 1.052    | w        |          |          |
| 1.710                                                       | vvw      | 1.690                                                                                | s        | 1.042    | m        |          |          |
| 1.696                                                       | w        | 1.642                                                                                | vw       | 1.024    | m        |          |          |
| 1.663                                                       | vvw      | 1.612                                                                                | ms       | 1.016    | w        |          |          |
| 1.607                                                       | vw       | 1.583                                                                                | m        | .951     | vw       |          |          |
| 1.522                                                       | w        | 1.553                                                                                | w        | .933     | w        |          |          |
| 1.405                                                       | vw       | 1.508                                                                                | w        | .919     | w        |          |          |
| 1.319                                                       | vw       |                                                                                      |          |          |          |          |          |
| 1.277                                                       | vw       |                                                                                      |          |          |          |          |          |
| 1.215                                                       | vw       |                                                                                      |          |          |          |          |          |
| .....                                                       | .....    |                                                                                      |          |          |          |          |          |

The first two analyses, of stones from a single occurrence, show the similarity to be expected; the most noticeable difference being in the content of  $\text{Na}_2\text{O}$ . Also to be expected is the similarity of these two analyses to that of a stone from the same kind of tree, though from a different locality (3). Further, the relation of these three analyses, to the fourth, of ash from wood of the same kind of tree, burned in the laboratory, is evident. The fifth analysis, of a stone from another type of tree, from a different part of the country, does not differ greatly, the variation being chiefly in  $\text{R}_2\text{O}_3\text{-P}_2\text{O}_5$  content. On the whole, the stones analyzed consist



of about two-thirds by weight of calcium and potassium carbonates. It may be here remarked that for the minor constituents, such as  $P_2O_5$ ,  $Al_2O_3 \cdot Fe_2O_3$ , and  $Mn_3O_4$ , no crystalline compound of them has been recognized in wood-ash stones. As for  $MgO$  and  $Na_2O$ , it is probable that they can enter isomorphously the double carbonates present, but such isomorphous replacement would not be shown by the methods employed in this study.

TABLE 2. ANALYSES. CHEMICAL COMPOSITION OF WOOD-ASH STONES, FAIRCHILDITE, AND BUETSCHLIITE

|                    | 1       | 2       | 3                     | 4     | 5            | 6     | 7     |
|--------------------|---------|---------|-----------------------|-------|--------------|-------|-------|
| $SiO_2$            | 0.32    | 0.38    | 0.41                  | —     | —            |       |       |
| $P_2O_5$           | 6.96    | 6.58    | 5.47                  | 10.5  |              |       |       |
| $Al_2O_3, Fe_2O_3$ | 1.68    | .99     | .34                   | 4.4   | 1.0          |       |       |
| $SO_3$             | tr.     | tr.     | .67                   | —     | .7           |       |       |
| Cl                 | tr.     | tr.     | tr.                   | —     | —            |       |       |
| CaO                | 22.02   | 21.90   | 21.79                 | 20.1  | 18.5         | 23.5  | 15.4  |
| MgO                | 6.28    | 4.48    | 4.06                  | 10.4  | 2.3          |       |       |
| $Mn_3O_4$          | 1.21    | 1.32    | 7.17                  | 11.7  | —            |       |       |
| $K_2O$             | 25.01   | 24.54   | 30.42                 | 34.9  | 23.6         | 39.5  | 39.1  |
| $Na_2O$            | 5.31    | 2.06    | 4.20                  | 8.0   | 10.7         |       |       |
| $CO_2$             | 19.76   | 25.47   |                       |       |              | 37.0  | 30.6  |
| $H_2O$             | } 11.65 | } 12.28 | } 25.47<br>(by diff.) | }     | 43.2 (calc.) |       | 14.9  |
| C, etc. (diff.)    |         |         |                       |       |              |       |       |
|                    | 100.00  | 100.00  | 100.00                | 100.0 | 100.0        | 100.0 | 100.0 |

1, 2. Fused wood-ash stone, Kaniksu National Forest, Coolin, Idaho (*tsuga heterophylla*, western hemlock). R. KIENHOLZ, *analyst* (2).

3. Fused wood-ash stone, Wind River Country, southern Washington (*tsuga heterophylla*, western hemlock). R. KIENHOLZ, *analyst* (2).

4. Ash of sound wood, Wind River Country, southern Washington (*tsuga heterophylla*, western hemlock). R. KIENHOLZ, *analyst* (2).

5. Fused wood-ash stone, Grand Canyon National Park, Arizona (*abies concolor*, white fir). C. MILTON, *analyst*.

6. Theoretical composition of fairchildite,  $K_2CO_3 \cdot CaCO_3$ .

7. Theoretical composition of buetschliite,  $3K_2CO_3 \cdot 2CaCO_3 \cdot 6H_2O$ .

#### ASH CONTENT OF WOOD IN RELATION TO STONE FORMATION

The quantity of ash that a given weight of dry wood will yield on burning is shown in Table 3.

The deciduous trees apparently give a higher ash content than the conifers. Further analyses of wood ashes may be found in Hagglund's treatise; here it need only be noted that all show predominant potash and lime.

As to the quantity of wood-ash stone that a single tree may yield, Kienholz (2) mentions "a hundred pounds or more." This is not excessive, as the following computation shows. Assuming 0.20% as the ratio of ash to wood, and 0.75 as an average for the density of the wood, a tree four feet in diameter and eighty feet high would yield a hundred pounds of ash. In considering Kienholz's figure, it should be mentioned that wood-ash stone differs from the true ash in containing a considerable quantity of combined carbon dioxide, water, and also perhaps charcoal; and furthermore, that a tree that is struck by lightning (which may have started

TABLE 3. PERCENTAGE OF ASH OBTAINED FROM DRY WOOD

|                         |      |               |
|-------------------------|------|---------------|
| Western hemlock         | .215 | Kienholz (2)  |
| European larch (splint) | .22  | Hagglund (10) |
| European larch (heart)  | .12  | Hagglund (10) |
| European pine (splint)  | .19  | Hagglund (10) |
| European pine (heart)   | .15  | Hagglund (10) |
| European fir (splint)   | .26  | Hagglund (10) |
| European fir (heart)    | .20  | Hagglund (10) |
| European oak (splint)   | .42  | Hagglund (10) |
| European oak (heart)    | .16  | Hagglund (10) |
| European beech (splint) | .47  | Hagglund (10) |
| European beech (heart)  | .40  | Hagglund (10) |

the fire in the tree) is likely to be among the tallest trees in its neighborhood. There is therefore no question of the adequacy of the quantity of ash available to produce such wood-ash stones as have been found.

#### CHEMISTRY OF THE SYSTEM $K_2CO_3$ - $CaCO_3$ - $H_2O$

Since wood-ash stones are composed mainly of these three compounds in various combination, the chemistry of their reactions with one another will be briefly discussed.

In 1894 H. Le Chatelier (11) had prepared in the dry way the anhydrous double carbonate of potassium and calcium. He described a series of compounds all apparently isomorphous, uniaxial negative, with excellent basal cleavage, and having the general formula  $R_2O \cdot RO \cdot 2CO_2$ , the univalent metals being sodium and potassium (but not lithium) and the bivalent metals being calcium, strontium, and barium. The various compounds were easily produced by fusion of the components. In his account

he refers to still earlier syntheses of these compounds by Berthelot.

The system  $\text{K}_2\text{CO}_3\text{-CaCO}_3$  was first studied by P. Niggli (12) in 1916. The double salt melts at  $815^\circ\text{C}$ . and forms a eutectic with  $\text{K}_2\text{CO}_3$  at  $455^\circ\text{C}$ ., or more precisely, with mixed crystals of  $\text{K}_2\text{CO}_3$  containing up to a little over 12% of  $\text{CaCO}_3$ . Above  $815^\circ\text{C}$ .,  $\text{CaCO}_3$  decomposes and it is therefore necessary to maintain an atmosphere of  $\text{CO}_2$  under pressure to prevent decomposition at temperatures higher than this. To synthesize the anhydrous double carbonate, however, the elaborate apparatus employed by Niggli and later workers is not needed, since, as shown by Le Chatelier, it is easily prepared by simple fusion of the two components in correct proportions, in an ordinary covered platinum crucible over a Meeker burner. In this way coarsely crystallized masses of a pinkish-gray color, showing excellent cleavages a centimeter or two across, are obtained. The compound is described as hexagonal, forming basal plates or masses with excellent basal cleavage, and having refractive indices  $\epsilon = 1.48$  and  $\omega = 1.530$ . Skalik (13) and later Eitel and Skalik (14) give the Laue x-ray pattern of the anhydrous double carbonate; the powder x-ray pattern, and measurements of the principal lines, are given in Table 1 and Fig. 6 of this paper.

However, Otto Buetschli, employing altogether different methods, had already in 1901 synthesized and identified the same compound. He observed that by treating calcareous sponge spicules with 35% KOH solution, hexagonal tablets crystallized. In his first published account of this work, in 1898 (15) he considered the possibility that they might be calcium carbonate; but later (16) showed that the crystals were decomposed by water, with formation of calcium carbonate. Therefore, he reasoned the tablets themselves could not be calcium carbonate, but had to be a double carbonate of potassium and calcium. His conclusions, however, were not accepted and several authorities raised objections.

The first to question Buetschli's findings was W. Biedermann (17). In 1901 he published his own observations, made independently of Buetschli. He too had observed the formation of hexagonal plates on treating calcareous mollusc shells with potash lye, and that these plates were decomposed by water, with formation of rhombohedral crystals. However, he misinterpreted the phenomena he observed, for he took the hexagonal plates to be calcium phosphate, which water caused to "recrystallize" into a rhombohedral form. In fact he believed that he had thus discovered a reaction for detecting minimal quantities of calcium phosphate.

That same year Buetschli reviewed Biedermann's work, pointed out his errors, and reiterated that a double carbonate of potassium and calcium was the compound in question (16).

In 1902 Biedermann found that the crystals were formed in the ab-



sence of any phosphate, by treating gaylussite (sodium calcium carbonate) with potash lye, or, calcium chloride or sulphate, with potash lye. He therefore withdrew his previous identification of the compound as calcium phosphate; but, without reference to Buetschli's work, observed that these crystals were to be classed as a potassium-calcium compound, whose composition was yet to be established.

Notwithstanding the clarity of Buetschli's published work, with its evident corroboration by Biedermann, O. Maas (18) in 1904 declared Buetschli's results altogether erroneous. According to him, 35% KOH had no effect at all, either on calcite or on freshly precipitated calcium carbonate. The sole effect on sponge spicules, he asserted, was to break up a single crystal spicule into an aggregate of smaller and diversely oriented calcite crystals; and the way this was done, was by the KOH dissolving a certain organic cement whose existence Buetschli had overlooked. The only new crystals that might be formed were those of potassium carbonate (by absorption of carbon dioxide from the air).

Buetschli considered all of Maas' statements and refuted them in a lengthy paper which appeared in 1905 (19). In it he presented analytical data from which he correctly deduced the composition not only of the anhydrous double carbonate (fairchildite) but also of a hydrous double carbonate (buetschliite). He gave a wealth of detail concerning the conditions of their formation, the form of their crystals, and further gave an extended discussion of related compounds, such as gaylussite and other hydrous sodium calcium carbonates, calcium phosphate, and hydrous calcium carbonate. He pointed out that Liebig, as far back as 1832, had shown that hot caustic potash attacks chalk, giving a soluble carbonate. In presenting his analyses, Buetschli modestly deprecated his ability as a chemist, observing that he had been unable to secure the help of an expert analyst, and therefore had to perform the analyses himself. However, his analyses, presented with most detailed explanation of all the analytical procedures employed, appear to be satisfactory in all respects; and his analysis giving the formula for the double hydrous carbonate (buetschliite) is accepted by the writers as correct.

Even while this paper of Buetschli's, which should have put an end to the controversy, was in the hands of the printer, there appeared, to his astonishment and dismay, a denial of the validity of its contents by no less an authority than Ernst Weinschenk (20). Weinschenk was Professor of Petrography at the University of Munich Mineralogical Institute, and an outstanding figure in mineralogy. He affirmed all of Maas' erroneous work and explicitly condemned that of Buetschli. More in sorrow than in anger, Buetschli took on this adversary, and in

the same journal that had published Weinschenk's attack, wrote a brief reply (21). To his still unpublished 1905 paper he added a long appendix, pointing out the errors and fallacies of Weinschenk's pronouncement. One sentence of Buetschli's may be quoted, as showing the spirit in which the controversy was carried on both sides. "Among other things, he derides me, because (he says) no such double salt as I have described is known, notwithstanding that potassium carbonate and calcium carbonate are substances that have been so completely investigated." On the other hand, Weinschenk claimed that the crystals which he himself (and Maas) had observed to form were simply anhydrous potassium carbonate, to which Buetschli dryly remarked that such a compound was not known to form in the wet way either; and then, by careful analysis, proved that the crystals produced in the course of Weinschenk's (and Maas') experiments, could not be other than  $2K_2CO_3 \cdot 3H_2O$ . In 1944 this was fully verified by Ervin, George, and McCarthy (22) who show that this hydrate is the only stable phase crystallizing from solution at all ordinary temperatures.

Finally in 1907 Buetschli (23) published his last work on these double carbonates. Most of the paper deals with gaylussite ( $Na_2CO_3 \cdot CaCO_3 \cdot 5H_2O$ ) and a (new) dehydration product  $Na_2CO_3 \cdot CaCO_3 \cdot 2H_2O$  but in his first paragraph he once more affirms that  $K_2CO_3 \cdot CaCO_3$  and  $3K_2CO_3 \cdot 2CaCO_3 \cdot 6H_2O$  crystallize when calcium carbonate reacts with a strong  $K_2CO_3$ -KOH solution.

Some years later Barre (24) also synthesized  $K_2CO_3 \cdot CaCO_3$ , obtaining acicular crystals by digesting precipitated  $CaCO_3$  in strong  $K_2CO_3$  solution. Water or solutions of potassium carbonate containing less than 59.25%  $K_2CO_3$  at 19° C. or 61.78% at 98° C. decompose the compound. Apparently Barre was unaware of Buetschli's prior work.

In 1913 Datta and Mukherjea (25) described the preparation of a compound reported to be  $3K_2CO_3 \cdot CaCO_3$ , but their account is not very convincing. They precipitated a jelly-like mass by adding concentrated calcium chloride solution to a saturated potassium carbonate solution; on standing this jelly formed crystals which were dried by suction without washing. Under these conditions it is difficult to see how adherence of potassium carbonate could be avoided. The composition of the crystals was determined solely by determination of the CaO content. The authors state that no water of crystallization was found, but this must be considered doubtful. Probably they were dealing with a mixture containing the hydrous double carbonate as well as potassium carbonate sesquihydrate.

The compounds in the system  $K_2CO_3$ - $CaCO_3$ - $H_2O$  which need be con-

sidered with reference to wood-ash stones are listed in the following table:

TABLE 4. COMPOUNDS OF  $K_2CO_3 \cdot CaCO_3 \cdot H_2O$  IN RELATION TO WOOD-ASH STONES

A. Compounds identified in wood-ash stones

$K_2CO_3 \cdot CaCO_3$ , Fairchildite; hexagonal, in basal plates with excellent basal cleavage.  $\epsilon = 1.48$ ;  $\omega = 1.530$  (-). Formed by fusion below  $815^\circ$  C. and also from concentrated aqueous solutions.

$3K_2CO_3 \cdot 2CaCO_3 \cdot 6H_2O$ , Buetschliite; hexagonal (probably) in stubby barrel-shaped crystals.  $\epsilon = 1.455$ ;  $\omega = 1.595$  (-). Formed by hydration of fairchildite, or by crystallization from less concentrated solutions.

$CaCO_3$ , Calcite; hexagonal.  $\epsilon = 1.491$ ;  $\omega = 1.658$  (-). Formed by decomposition of buetschliite by water, and also in the hydration of fairchildite.

B. Compounds which may have a transient existence in wood-ash stones, but by their extreme solubility or unstable chemical character, are not likely to be recognized or present.

$K_2CO_3$ , monoclinic;  $\alpha = 1.426$ ;  $\beta = 1.531$ ;  $\gamma = 1.541$  (-).  $2V = 35^\circ$ , lamellar twinning, oblique extinction. Made by fusion of hydrates; not known as a mineral.

$2K_2CO_3 \cdot 3H_2O$ , monoclinic;  $\alpha = 1.474$ ;  $\beta = 1.483$ ;  $\gamma = 1.510$  (+).  $2V = 66^\circ$ , extinction  $15^\circ$ - $20^\circ$ . This is the stable phase crystallizing from aqueous solutions at ordinary temperatures.

$CaO$ , Lime; cubic;  $n = 1.837$ ; perfect cubic cleavage. Hydrates rapidly in air.

$Ca(OH)_2$ , Portlandite; hexagonal;  $\epsilon = 1.545$ ;  $\omega = 1.574$  (-); basal cleavage. Made by hydration of lime out of contact with  $CO_2$  (or air).

### NEW MINERAL NAMES: FAIRCHILDITE AND BUETSCHLIITE

The names chosen to designate these naturally occurring double carbonates are in honor of our co-worker, John G. Fairchild, chemist of the Geological Survey, United States Department of the Interior, and of Otto Buetschli (1848-1920), professor of zoology at the University of Heidelberg from 1878 to 1919. John G. Fairchild has for over thirty years devoted his analytical skill to the study of geochemical problems. Otto Buetschli, although a zoologist, and not a chemist, was the first to synthesize, and to correctly understand the relations of both fairchildite and the compound now named after him. His findings were sharply challenged during his lifetime, but the present study must be regarded as completely vindicating his work. It is also worth a moment's reflection, to recall that it was the work of an investigator in Germany, primarily concerned with the morphology of sponge skeletons, that was to be the key to the understanding of puzzling stones found after forest fires in western American forests. It is but another illustration, if such were needed, that no one may prescribe the results or possible applications of free scientific inquiry.



## ACKNOWLEDGMENTS

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Microscopic study of these stones was made possible through the skill of Frank Reed and John Mergner, technicians of the Geological Survey, who prepared excellent thin sections of this difficult material.

W. T. Schaller, (former) Chief Chemist, Earl Ingerson, Chief Chemist, and C. S. Ross, (former) Chief Petrologist of the Geological Survey, have critically read and constructively commented on the manuscript.

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# INVESTIGATION OF THE MICACEOUS MINERALS IN SLATE

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## ABSTRACT

A mineral of the illite (hydromica) group forms the bulk of the fine micaceous material in the slates from the Lehigh-Northampton district of northeastern Pennsylvania. Although similar to the type illite from Fithian, Illinois, in all other respects, electron microscope studies reveal that the mineral in the slate occurs in flakes which morphologically are larger and much better defined than the fuzzy aggregates of minute shreds or fibers which characterize electron micrographs of illite obtained from shales. X-ray orientation studies show that the flakes are arranged in parallel orientation in the slate and that the amount of alignment is related to the degree of metamorphism. In the specimens studied the development and alignment of illite plates by metamorphic processes is believed to be the cause of slaty cleavage.

Concentrates of the illite mineral were obtained by froth flotation and supercentrifuge techniques. Due to the presence in the slate of sericite and chlorite, a number of methods were used to determine the nature of the mineral in the fine fractions. Although chemical analyses and thermal tests are particularly diagnostic, data provided by x-ray units, the petrographic microscope, and the electron microscope are also significant.

## INTRODUCTION

As part of a project of the Mineral Industries Experiment Station of The Pennsylvania State College investigating the nature and future utilization of slate, thorough studies of the minerals have been made. While much of the mineralogy of slate has been discussed (1, 2, 3, 4, 5), this investigation has revealed interesting facts pertaining to a number of the minerals in slate and particularly to the micaceous minerals.

The samples studied were from the Lehigh-Northampton slate belt of northeastern Pennsylvania. Detailed investigations were made of a typical slate from the Parsons Brothers slate quarry on the Diamond Vein at Pen Argyl, and other slates were compared with this as a standard.

The investigation was made largely with the petrographic microscope and x-ray diffraction units, but firing tests, differential thermal analyses, chemical analyses, and electron micrographs and diffraction photographs have provided much of the significant data.

When the study was begun, microscopic work indicated that the cleavage of this slate was due to a mineral of the illite (hydromica) group. Such a possibility had been suggested by Fairbairn (5) as the result of x-ray studies of foliated rocks. Figure 1 is a photomicrograph of a slate section cut perpendicular to the cleavage. The dark veinlets are com-



posed of minute shreds and fibers individually half a micron or less in width. These tiny fragments are subparallel with a prominent cleavage parallel to the foliation of the rock. They show optical orientation which is easily recognized by a marked increase in absorption when the veinlets are parallel to the vibration direction of the incident polarized light. Larger sericite and chlorite flakes are easily distinguished but the mineral



FIG. 1. Photomicrograph of slate, section cut perpendicular to cleavage ( $\times 175$ ).

forming the veinlets differs from sericite in color and pleochroism, and from chlorite in birefringence. The investigation has not only shown that the mineral is a member of the illite group but has furnished data of possible significance in the interpretation of the mineralogical changes which accompany the development of slaty cleavage during metamorphism.

#### SAMPLE PREPARATION

In addition to the micaceous minerals, the slate contains quartz, calcite, dolomite, feldspar, pyrite, rutile, graphite, and carbonaceous matter. In consequence, one of the main problems in the detailed study of any single mineral was to separate it from the others. This was particularly difficult in the case of the illite mineral because the flakes of sericite and chlorite range from less than five to more than 500 microns in length. It

was found that pure fractions of the unknown could not be obtained in sufficient quantity to justify the time expended, but by a combination of methods, relatively pure concentrates of the micaceous minerals could be made.

Slate "flour" was used in all fractionation work. 85% of this material is finer than 0.044 mm. since it will pass a 325 mesh sieve whereas all of it goes through a 200 sieve with an opening of 0.074 mm. The pyrite and carbonaceous matter were first removed by froth flotation in a 500 gram Fagergren cell. To 450 grams of slate 50 mg. of potassium ethyl xanthate

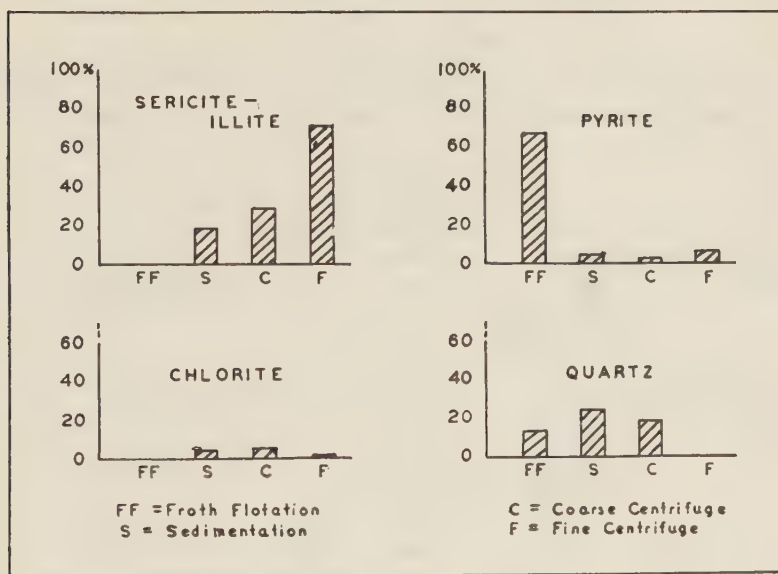


FIG. 2. Concentrates obtained by fractionation of slate.

was added to act as a collector for pyrite while three drops of pine oil and one of mineral oil served as flotation reagents for the carbonaceous material. The pine oil also acted as a frother. The froth was collected and the remainder of the material dispersed by adding 250 mg. of sodium lignin sulphonate. After dispersion, the preparation was allowed to settle until particles 50 microns or less were the only ones still in suspension.

Further fractionation was made with the Sharples supercentrifuge. Several fractions were obtained by varying the speed and the rate of the feed. For detailed information on the use of this method reference may be made to papers by Fancher and Oliphant (6) and by Oliphant, Houssiere, and Fancher (9). Figure 2 shows the approximate percentage of some of

the minerals in several of the fractions. Since the percentages were obtained by x-ray methods no attempt was made to distinguish between sericite and illite in the histogram. The concentrate of fine grained mica-ceous material provided by the fine centrifuge fraction was found to be of sufficient purity to permit detailed study of the mineral in question.

Using this fraction, tests were made comparing the concentrate with varieties of chlorite and sericite, and with the illite mineral from Fithian, Illinois, described by Grim, Bray, and Bradley (7). Due to the presence of sericite and chlorite and the frequent similarity in behavior of these minerals to that of illite the results were checked by a number of methods.

### MICROSCOPIC DATA

Table 1 compares the optical data of sericite, chlorite, and type illite with that of the unknown. Since the chlorite in the slate is apparently the

TABLE 1. MICROSCOPIC DATA

|                           | Color                              | Orientation                  | Absorption  | $n_{\gamma}$ | $n_{\gamma} - n_{\alpha}$ |
|---------------------------|------------------------------------|------------------------------|-------------|--------------|---------------------------|
| ILLITE                    | Gray<br>Light Green<br>Light Brown | $X \wedge c = 0^{\circ} \pm$ | X and Y < Z | 1.588-1.610  | .033-.035                 |
| CONCENTRATE<br>from slate | Gray<br>Green                      | $X \wedge c = 0^{\circ} \pm$ | X and Y < Z | 1.587-1.602  | .027-.032                 |
| SERICITE                  | Colorless<br>Pale Green            | $X \wedge c = 0^{\circ} \pm$ |             | 1.593-1.611  | .037-.041                 |
| CHLORITE<br>(penninite)   | Green                              | $Z \wedge c = 0^{\circ} \pm$ | X and Y > Z | 1.576-1.583  | .001-.004                 |

penninite variety the tabulated figures apply to this species. Attempts to obtain the diagnostic interference figure on oriented aggregates were unsuccessful, but pronounced absorption in addition to marked birefringence suggest that the material is illite rather than sericite or chlorite.

### X-RAY STUDY

As Grim et al. (7) have pointed out, there is no significant variation in the interplanar spacings of muscovite, sericite, and illite, although the unit cell appears to be slightly larger in the case of illite. The breadth of the diffraction lines increases from muscovite to illite and this criterion may be employed provided it is kept in mind that the difference may be in part or entirely due to variation in particle size. Figure 3 shows how a



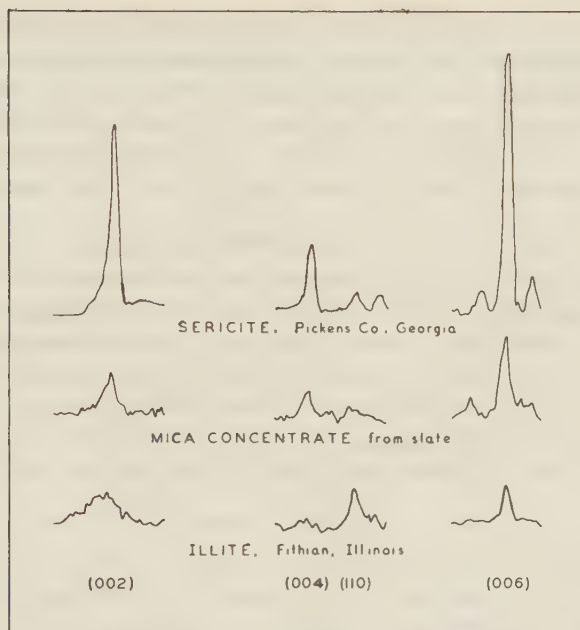


FIG. 3. X-ray spectrometer patterns.

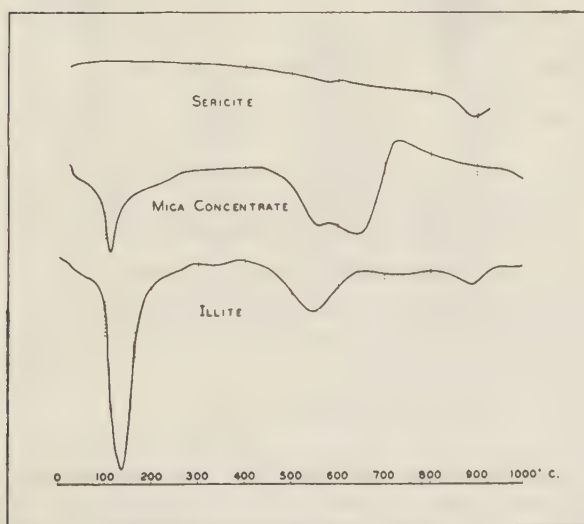


FIG. 4. Differential thermal analysis curves.

pattern made with the Norelco *x*-ray spectrometer compares with similar patterns of illite and sericite. Thus, although the mica concentrate resembles the illite more than the sericite, the somewhat sharper peaks may represent: (1) coarse-grained illite; (2) very fine-grained sericite; or (3) a mixture of sericite and illite. X-ray diffraction data shows that chlorite is present in the fine concentrate but only in small amount.

#### DIFFERENTIAL THERMAL ANALYSES

Figure 4 shows differential thermal analysis curves of the known and unknown materials. Since *x*-ray study shows no indication of endellite or any mineral of the montmorillonite group, the low temperature endothermal peak together with the reaction at 560° C. indicates that there is appreciable illite in the fine fraction from the slate. The peak at 640° C. is probably due to the presence of chlorite (10) since even small amounts can give a large endothermal reaction in this temperature range.

#### FIRING TESTS

The effect of heat upon the minerals was also studied by firing them to different temperatures and noting changes in structure and the new minerals formed. The procedure consisted of heating a group of samples to a given temperature, allowing them to remain there for two hours, and

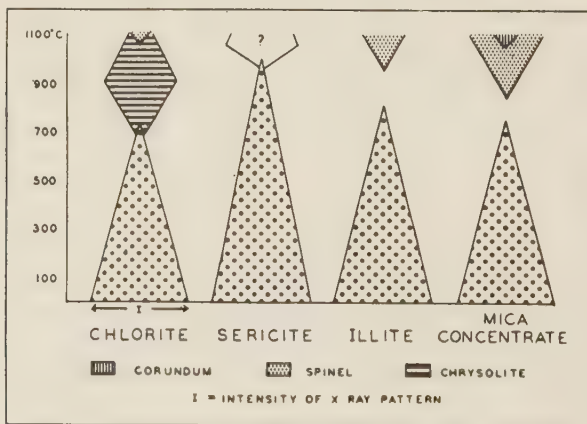


FIG. 5. Firing Data.

then removing them from the furnace to permit rapid cooling. A new group of specimens from the original set of samples was used for each firing and the temperatures were 250, 600, 650, 900, 1000, 1100 degrees Centigrade. After cooling each specimen was studied microscopically and

$x$ -rayed. Figure 5 summarizes diagrammatically the data obtained and shows the similarity in behavior of the fine slate fraction to the illite mineral from the type locality. In the figure the width of each area represents the intensity of the  $x$ -rays diffracted by the phase which exists at the given temperature.

### CHEMICAL ANALYSES

Chemical analyses support the evidence that most of the fine fraction from the slate is an illite mineral rather than sericite. Analyses of the mica concentrate and of illite are given in Table 2 and the diagnostic ratios are shown in Table 3. Since  $\text{TiO}_2$  and probably  $\text{CaO}$  are present as

TABLE 2. CHEMICAL ANALYSES

|                                                   | 1      | 2       | 1-R     | 2-R     |
|---------------------------------------------------|--------|---------|---------|---------|
| $\text{SiO}_2$                                    | 45.65% | 48.95%  | 47.76%  | 48.25%  |
| $\text{Al}_2\text{O}_3$                           | 25.05  | 25.03   | 26.13   | 24.69   |
| $\text{Fe}_2\text{O}_3$                           | 5.41   | 7.29    | 5.66    | 7.20    |
| $\text{FeO}$                                      | —      | 1.61    |         | 1.59    |
| $\text{TiO}_2$                                    | 1.95   | 0.51    |         |         |
| $\text{CaO}$                                      | 1.59   | 0.29    |         |         |
| $\text{MgO}$                                      | 3.40   | 3.10    | 3.56    | 3.05    |
| $\text{Na}_2\text{O}$                             | 0.51   | 0.15    | 0.53    | 0.15    |
| $\text{K}_2\text{O}$                              | 6.50   | 6.03    | 6.81    | 5.95    |
| $\text{H}_2\text{O}$ at $110^\circ \text{C}$ .    | 0.60   | 1.70    | 0.63    | 1.67    |
| $\text{H}_2\text{O}$ above $110^\circ \text{C}$ . | 8.53   | 7.56    | 8.92    | 7.45    |
| Total                                             | 99.19% | 102.22% | 100.00% | 100.00% |

1. Concentrate from slate: Analyzed by R. J. Grace, School of Mineral Industries, The Pennsylvania State College.

2. Illite: Average of five analyses, Grim et al. (7).

1-R. Analysis #1 minus  $\text{TiO}_2$  and  $\text{CaO}$  and recomputed to 100%.

2-R. Analysis #2 minus  $\text{TiO}_2$  and  $\text{CaO}$  and recomputed to 100%.

TABLE 3. DATA FROM CHEMICAL ANALYSES

|                           | $\text{SiO}_2/\text{K}_2\text{O}$ | $\text{SiO}_2/\text{R}_2\text{O}_3$ | $\text{R}_2\text{O}_3/\text{K}_2\text{O}$ | $\text{SiO}_2/\text{Al}_2\text{O}_3$ |
|---------------------------|-----------------------------------|-------------------------------------|-------------------------------------------|--------------------------------------|
| 1. Muscovite              | 6.0                               | 2.0-2.56<br>average: 2.4            | 2.35-3.10<br>average: 2.80                | 1.0-3.0                              |
| 2. Concentrate from slate | 11.05                             | 2.74                                | 4.04                                      | 3.11                                 |
| 3. Illite                 | 12.75                             | 2.80                                | 4.56                                      | 3.32                                 |

1. Hallimond, A. F. (8).

2. From analysis 1-R, Table 2.

3. From analysis 2-R, Table 2.



impurities, the original analyses 1 and 2 have been recomputed without these constituents in order to better represent the chemical nature of the illite and the mineral forming the slate concentrate.

#### ELECTRON MICROSCOPE STUDY

From the foregoing data, particularly that supplied by chemical analyses, firing tests, and differential thermal analyses, it seems evident

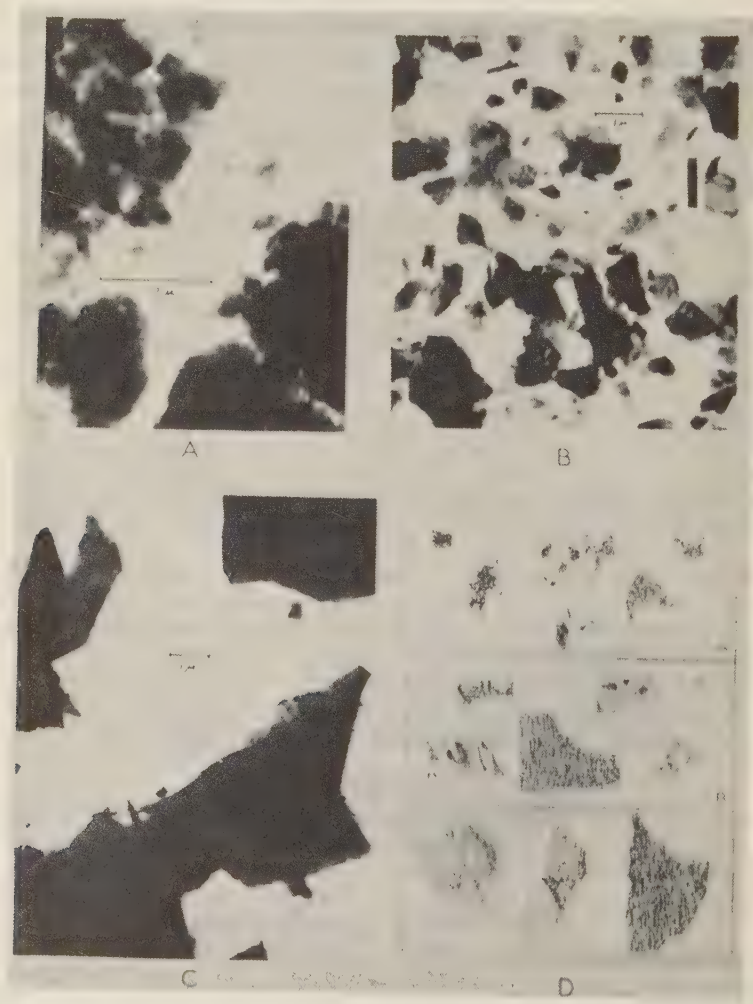


FIG. 6. Electron micrographs. A. Illite mineral from shale, Fithian, Illinois. B. Illite mineral from slate, northeastern Pennsylvania. C. Sericite, Pickens County, Georgia. D. Sketch of characteristic particles from A, B, and C.

that a member of the illite group forms the bulk of the fine slate fraction and is the mineral forming the veinlets shown in Figure 1. Sericite and chlorite apparently account for only a small percentage of the fine micaceous material although larger grains of these minerals are common. In consequence, the electron micrographs in Fig. 6 are of particular interest since the shreds in the picture of the slate fraction do not resemble the fibrous aggregate typical of illite from shale but are similar to sericite both in shape and structure, although smaller in size. Since this mineral differs from type illite only in morphology, it is logical to assume that the development of larger, well-defined flakes is a result of metamorphism.

#### ORIENTATION DATA

In order to better understand the effect of metamorphism upon the illite, orientation studies have been made upon two slates, one from the "soft-slate" belt from which all slate for commercial use is taken at the present time, the other from the adjacent "hard-slate" belt where the

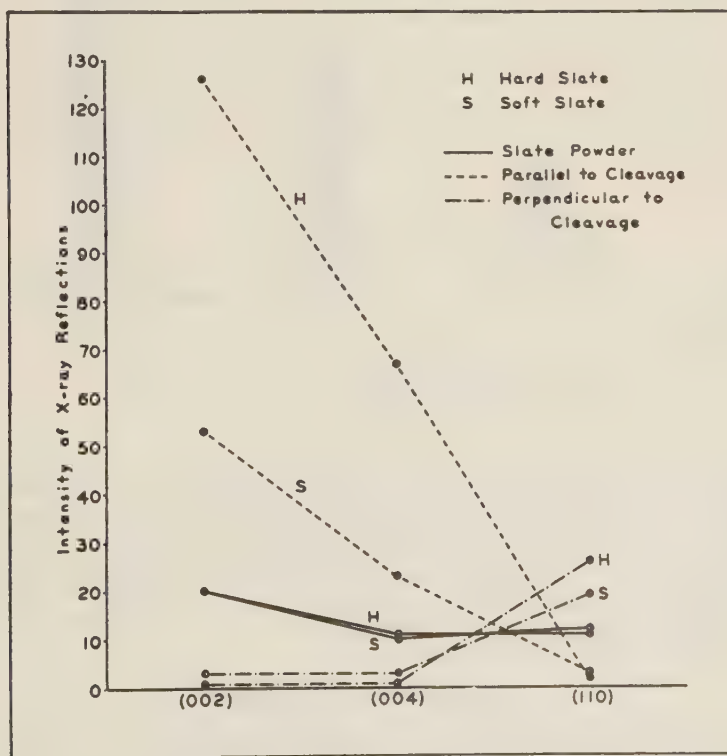


FIG. 7. Orientation study of slate.

rock is much more fissile as a result of a greater degree of metamorphism. The degree of orientation of the illite shreds is shown by Geiger counter measurements of  $x$ -ray reflections from the (001) and (110) planes of the illite in slate sections cut both parallel and perpendicular to the cleavage. Data presented in Fig. 7 show that in slate sections cut parallel to the cleavage, reflections from the (001) illite planes are very strong while (110) reflections are weak, while in sections cut perpendicular to the

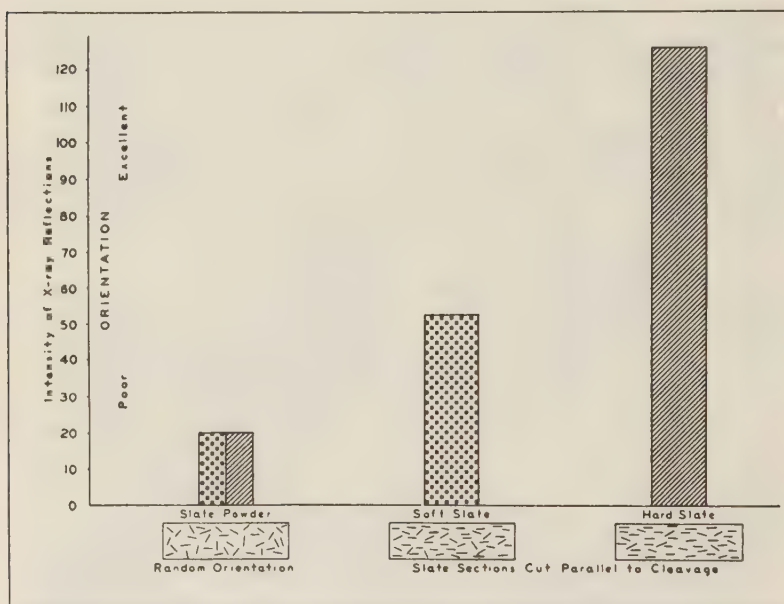


FIG. 8. Degree of orientation of (001) planes of illite in cleavage plane of slate.

cleavage the opposite is true. Since the particle size in the two slates is nearly the same, the difference in intensity of reflections from the same set of planes is an indication of the degree of orientation in the two slates. Figure 8 shows that in proportion to every five illite shreds in the hard slate that are oriented with (001) parallel to slate cleavage only two shreds are so oriented in the soft slate.

#### INTERPRETATION OF DATA

It is not known whether the illite mineral in the slate was developed from micas and clay minerals during metamorphism or whether illite was present in the original shale and has simply been recrystallized. In either



case the effect of metamorphism was twofold: (1) well defined micaceous plates of illite were developed, and (2) presumably during their development, these plates were arranged with basal planes in parallel orientation.

Thus, in the specimens studied, it seems probable that slaty cleavage is caused by the parallel alignment of illite plates. Each dark "veinlet" seen in Fig. 1 is the edge of a broad sheet made up of innumerable parallel flakes. The cleavability of a particular slate sample depends directly upon the number, morphology, and especially the degree of alignment of these minute particles.

#### SUMMARY

Although optical and x-ray studies are not conclusive, chemical analysis and thermal tests indicate that a mineral of the illite (hydromica) group is a major constituent of the slates of northeastern Pennsylvania. Electron micrographs reveal that the illite from the slate resembles sericite in that it is more coarsely crystalline and platy than typical illite obtained from shale, the difference apparently being due to metamorphism. In the "hard slate" which has undergone a greater degree of metamorphism than the adjacent "soft slate," the plates are more perfectly oriented with the (001) planes parallel. In the specimens studied the development and alignment of illite plates by metamorphic processes is believed to be the cause of slaty cleavage.

#### ACKNOWLEDGMENT

Throughout the study the writer was ably assisted by many members of the staff of the School of Mineral Industries of The Pennsylvania State College. In particular, Mr. Herbert Kellogg, former Chief of the Mineral Preparation Division, helped with the fractionation of the slate; Dr. Samuel Zerfoss rendered much helpful advice in connection with the heat treatment of the specimens; Mr. Robert Gruver made most of the differential thermal analyses. Mr. Howard K. Lucas assisted with much of the work and made many valuable suggestions. In the electron microscope work the author was assisted by Mrs. Elizabeth Hartner and Mrs. Mary V. Black.

The mineralogical concepts evolved during the investigation were frequently discussed with Dr. Paul Krynine, Chief of the Division of Mineralogy, who gave much of his time in order to help with both the interpretation and the presentation of the data. In addition, valuable advice on many aspects of the study was offered by Dr. Herbert Insley, former Head of the Department of Earth Sciences, and by Professor E. C. Henry, Chief of the Division of Ceramics.

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# REEXAMINATION OF SPHENE (TITANITE)<sup>1</sup>

HOWARD W. JAFFE<sup>2</sup>

## ABSTRACT

Sphene (titanite) invariably contains a minor amount of fluorine, as well as varying amounts of  $R_2O_3$ . R includes Fe, Al, Y and Ce. On the basis of similarities of ionic radii, trivalent Cr and quinquevalent Cb may be expected to proxy for quadrivalent Ti. An occurrence of a chromiferous sphene from California is described. The presence of Cb in sphene is verified.

## GENERAL

A portion of the data included in this paper was originally incorporated into a manuscript completed in July 1946. Shortly thereafter some additional data on sphene was obtained and necessitated a revision of and an addition to the original manuscript. Upon completion of this second manuscript, it was learned that Th. G. Sahama had been engaged in a similar study in Helsinki, Finland, and had published a paper, "On the Chemistry of the Mineral Titanite," in the *Bulletin de la Commission Geologique de Finlande*, N:o 138, 1946. Although this paper was not available to American readers until very recently, Dr. Sahama's priority in this study is apparent. Consequently, a section on the isomorphous replacements in sphene has been deleted from the present paper in deference to Sahama's very thorough treatment of the subject.

Although several of the writer's findings are similar to those of Sahama, the studies were made of sphenes and keilhauites from different localities than those described by him. The six sphenes described by Sahama are all from Finnish or Russian localities, whereas the sixteen sphenes described by the present writer are representative of a more world-wide distribution of this mineral. The significance of two independent investigations of different samples of sphene leading to similar analytical results and theoretical conclusions is apparent.

## FLUORINE IN SPHENE

During a routine visual spectroscopic examination of sphene, it was observed that the mineral contained fluorine. After microscopic examination showed the sample to be homogeneous, sixteen additional samples of sphene were examined in a like manner. All were found to contain fluorine in minor amounts. Most of the samples were furnished through

<sup>1</sup> Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior.

<sup>2</sup> Chemist-Petrographer, Metallurgical Branch, College Park Division, Bureau of Mines, College Park, Maryland.



the courtesy of the U. S. National Museum and the Harvard University Geological Museum.

A very rapid and an exceedingly sensitive qualitative method for detecting fluorine in minerals is that of visual arc spectroscopy. This method was described by Papish, Hoag and Snee (1930) and more recently by Peterson, Kauffman and Jaffe (1947). Fluorine may be readily detected spectroscopically, provided the sample contains calcium. When both elements are present and the sample is subjected to arc excitation, visual observation of the calcium fluoride band serves for the detection of fluorine. The band has its maximum or head at 5291 Å and fades toward the red or long wavelength portion of the spectrum. If the mineral does not contain calcium, any pure salt of calcium may be added. In such instances the salt should first be examined spectroscopically in order to determine that fluorine is not present as an impurity. Recent studies indicate that under normal operating conditions, the visual method is more sensitive than the photographic plate, as regards the detection of calcium fluoride. Papish, Hoag and Snee (1930) state that the calcium fluoride band cannot be detected in the arc spectrum (presumably the spectrogram) of topaz without the addition of a calcium salt. The writer recently examined samples of topaz from Nigeria, Brazil, Connecticut, Virginia and North Carolina and was able to detect the calcium fluoride band in all five samples by visual spectroscopic examination and without the addition of a calcium salt. Similarly, the band was observed in samples of amblygonite, muscovite, biotite, and wavellite. Apparently a small amount of calcium is present as an impurity in all of these minerals. Fluorine in minerals may be detected by this method in concentrations of less than 0.1 per cent.

Following the detection of fluorine in all sixteen samples of sphene and keilhauite, five of these were analyzed quantitatively by means of the Willard-Winter distillation method. The five samples analyzed were selected to represent widely scattered localities. The results of the analyses are given in Table 1.

Whether a small amount of fluorine is essential for the formation of

TABLE 1. FLUORINE CONTENT OF SPHENE

| Locality                 | F    |
|--------------------------|------|
| 1. Bancroft, Ontario     | 0.47 |
| 2. Midongy, Madagascar   | 0.68 |
| 3. Natural Bridge, N. Y. | 0.12 |
| 4. Delaware County, Pa.  | 0.16 |
| 5. Arendal, Norway       | 0.35 |

sphene is questionable. Mellor (1930) notes that sphene is not easily synthesized but lists several investigators who claim to have done so. The possibility exists that the constituents used in the syntheses contained a minor amount of fluorine as an impurity.

Sphene occurs in a wide variety of rocks and the presence of fluorine is not necessarily attributed to pegmatitic activity. It is found in igneous and metamorphic rocks and to a lesser extent as a detrital mineral. Host rocks include syenite, nepheline syenites, phonolite, monzonite, granite, talc schist, mica slate, tactite, skarn, metamorphosed limestone, chlorite schist and amphibolite. Fluorine was detected in samples of sphene occurring in syenite (#15—Table 3); in tactite (#13—Table 3); in chlorite schist (#5—Table 3); and in a detrital heavy mineral sand (#12—Table 3).

#### $R_2O_3$ IN SPHENE

Sphene has long been known to contain varying amounts of  $R_2O_3$  with  $R = Fe, Al, Y$  and  $Ce$  replacing calcium and titanium. Where the substitution becomes significant, the varietal names kielhauite and yttrotitanite are sometimes used. In recent years, it has been shown that sphene and keilhauite have virtually identical  $x$ -ray diffraction patterns (Young, 1938, and Kauffman and Jaffe, 1946) although the axial angles and refractive indices may show slight to moderate variation. According to Goldschmidt (1945) and others, large-scale isomorphous substitution in minerals may take place most readily where the pairs of ions involved have similar ionic radii. For a thorough study of the isomorphous mixtures encountered in sphene, the reader is referred to the very recent paper by Sahama (1946). In brief review we find that  $Ca^{++}$  and  $Y^{+++}$  both have ionic radii of 1.06 Å. and might be expected to replace one another in sphene. Similarly,  $Fe^{+++}$  and  $Al^{+++}$  have ionic radii of 0.67 Å. and 0.57 Å., respectively, and may proxy for  $Ti^{++++}$ , which has an ionic radius of 0.64 Å. Sahama notes the following replacements found in sphene.

“Calcium: Na, Rare Earths, Mn, Sr, (Ba).

Titanium: Al, Fe (ferric and ferrous), Mg, Nb, (Ta), V, (Cr).

Oxygen: OH, F, (Cl?).”

Chromium, placed in parentheses, was reported in two of his six analyses; 0.01 per cent  $Cr_2O_3$  in Analysis 2 and 0.02 per cent in Analysis 3. He calculates that if the abundance relation of titanium to chromium in the sphene lattice was the same as in the igneous rocks in average, this mineral would contain as much as 1.6 per cent  $Cr_2O_3$ . Sahama concludes that, in spite of the small number of determinations, this figure is at best a theoretical value and apparently is high.

An unusual instance of the substitution of trivalent Cr (0.64 Å) for

quadrivalent Ti ( $0.64 \text{ \AA}$ ) may be cited in support of Sahama's calculations. A sample of sphene in a tactite recently submitted to the Eastern Experiment Station, College Park, Maryland, has a  $\text{Cr}_2\text{O}_3$  content of 0.3–0.8 per cent. The sample was sent by J. M. Musgrave of Pasadena, California, who states that it occurs in "the southern California desert area." Further field information was not given.

The tactite contains several small grass-green crystals of chromiferous sphene. These have an average grain diameter of 0.5 mm. and are imbedded in a matrix of buff idocrase and gray-green diopside. Several grains of deep emerald green uvarovite are present. These show a maximum size development of 10 mm.

In plane-polarized light, the sphene shows a marked pleochroism, with X colorless, Y pale yellow-green, and Z grass-green. The intermediate index is 1.91 and the birefringence equal to 0.12. The mineral is optically positive with  $2V$  equal to approximately  $35^\circ$ . Dispersion is strong with  $r > v$ .

Not enough pure material could be selected for a quantitative chemical analysis. Spectrographic analysis, however, shows that the  $\text{Cr}_2\text{O}_3$  content lies in the range of 0.3 to 0.8 per cent. An x-ray powder diffraction pattern obtained with Cu radiation proved to be identical with that of normal sphene.

#### COLUMBIUM IN SPHENE

An additional minor element found in some samples of sphene is columbium. Eight of the sixteen samples examined spectroscopically contained this element. Quinquevalent Cb having an ionic radius of  $0.69 \text{ \AA}$  should be expected to substitute for quadrivalent Ti with a radius of  $0.64 \text{ \AA}$ . Four of these samples were analyzed spectrographically. The results are given in Table 2.

TABLE 2. COLUMBIUM CONTENT OF SPHENE (SPECTROGRAPHIC)

| Locality                    | $\text{Cb}_2\text{O}_5$ |
|-----------------------------|-------------------------|
| 1. Bancroft, Ontario        | 0.1–1.0                 |
| 2. Midongy, Madagascar      | 0.05–0.5                |
| 3. S. W. Africa (Kahn Mine) | 0.1–1.0                 |
| 4. Arendal, Norway          | 0.1–1.0                 |

#### CONCLUSIONS

As pointed out by Young (1938) and recently emphasized by Sahama (1946), many analyses of sphene are in the neighborhood of 50 years old



and in many of these only the three constituents,  $\text{CaO}$ ,  $\text{TiO}_2$  and  $\text{SiO}_2$  were determined. As is shown in Table 3, ferric iron, alumina and fluorine are commonly present in sphene and frequently are not reported by analysts. In the light of recent studies, it appears that the generally accepted but old formula,  $\text{CaTiSi}_2\text{O}_6$ , needs revision. Accordingly the following more inclusive formula is offered for sphene:  $(\text{Ca}, \text{X}) (\text{Ti}, \text{Z}) \text{Si}_2 (\text{O}, \text{OH},$

TABLE 3. VISUAL SPECTROSCOPIC ANALYSES OF SPHENE

| Locality                                                       | CaO | TiO <sub>2</sub> | SiO <sub>2</sub> | F | Fe <sub>2</sub> O <sub>3</sub> | Al <sub>2</sub> O <sub>3</sub> | Ch <sub>2</sub> O <sub>5</sub> | R.E.* | Cr <sub>2</sub> O <sub>3</sub> |
|----------------------------------------------------------------|-----|------------------|------------------|---|--------------------------------|--------------------------------|--------------------------------|-------|--------------------------------|
| 1. Delaware Co., Pa.<br>(N.M. 92843)                           | M   | M                | M                | m | m                              | m                              | —                              | —     | —                              |
| 2. North Carolina<br>(N.M. 48811)                              | M   | M                | M                | m | m                              | m                              | —                              | —     | —                              |
| 3. Ontario<br>(N.M. 97487)                                     | M   | M                | M                | m | m                              | m                              | —                              | —     | —                              |
| 4. Kola, U.S.S.R.<br>(N.M. 103300)                             | M   | M                | M                | m | m                              | m                              | m                              | m     | —                              |
| 5. Washington, D. C.<br>(N.M. 45848)                           | M   | M                | M                | m | m                              | m                              | —                              | —     | —                              |
| 6. Askero, Norway<br>(N.M. R7134)                              | M   | M                | M                | m | m                              | m                              | m                              | m     | —                              |
| 7. Arendal, Norway<br>(N.M. 49019)—var. keilhauite             | M   | M                | M                | m | m                              | m                              | m                              | m-M   | —                              |
| 8. Natural Bridge, N. Y.<br>(N.M. C3921)                       | M   | M                | M                | m | m                              | m                              | —                              | —     | —                              |
| 9. Midongy, Madagascar<br>(H.M. 88743)                         | M   | M                | M                | m | m                              | m                              | m                              | m     | —                              |
| 10. Arendal, Norway<br>(H.M. 87737)—var. keilhauite            | M   | M                | M                | m | m                              | m                              | m                              | m-M   | —                              |
| 11. S. W. Africa (Kahn Mine)**<br>(H.M. 89494)—var. keilhauite | M   | M                | M                | m | m                              | m                              | m                              | m     | —                              |
| 12. El Dorado Co., Calif.<br>(C.P. A209)                       | M   | M                | M                | m | m                              | m                              | —                              | —     | —                              |
| 13. S. California<br>(C.P. A209-a)                             | M   | M                | M                | m | m                              | m                              | —                              | —     | m                              |
| 14. Kragero, Norway<br>(C.P. A208)                             | M   | M                | M                | m | m                              | m                              | m                              | m     | —                              |
| 15. Bancroft, Ontario<br>(C.P. A208-a)                         | M   | M                | M                | m | m                              | m                              | m                              | m     | —                              |
| 16. N. Y.<br>(C.P. 323)—var. yttrotitanite                     | M   | M                | M                | m | m                              | m                              | —                              | m     | —                              |

\* R.E. = Rare Earths, mostly  $\text{Y}_2\text{O}_3$  and  $\text{Ce}_2\text{O}_3$  N.M. = National Museum

M = Major constituent

H.M. = Harvard Museum

m = Minor constituent

C.P. = College Park Petrographic Lab.

\*\* Contains an opaque Cu mineral.

F)<sub>5</sub>, where X = Y, Ce, Na, Mn, Sr, (Ba) and Z = Fe, Al, Cr, Cb, (Ta), V, Mg.

#### ACKNOWLEDGMENT

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# QUARTZ PARAMORPHS AFTER TRIDYMITE FROM COLORADO\*

LOUIS L. RAY

## ABSTRACT

Tabular quartz phenocrysts as much as 17 mm. in diameter, paramorphs after tridymite, occur in a small intrusive body of quartz latite porphyry at Home, Colorado. Studies of the quartz phenocrysts show that the optic axis tends to make an angle of  $61^\circ$  to the normal to the plates.

## INTRODUCTION

Approximately 500 feet north of Colorado State Highway 14, at Home, Colorado, on the north wall of the Cache la Poudre Valley (Home Quadrangle), a small body of quartz latite porphyry has been intruded into the pre-Cambrian basement complex. Although similar intrusive bodies are common throughout the Southern Rocky Mountains, that at Home is of especial interest because of the unusually large tabular phenocrysts of quartz which are paramorphs after tridymite. Studies of the phenocrysts indicate a lack of a simple, systematic orientation of the optic axis with respect to the tabular form of the paramorphs.

Specimens were first studied in the laboratories of Prof. E. S. Larsen at Harvard University. His continued interest and direction have resulted in this report; his aid is gratefully acknowledged.

## CHARACTER OF INTRUSIVE ROCK

In the hand specimen the quartz latite porphyry of the Home intrusive has a well-developed porphyritic texture (Fig. 1) with a micro-granular, light bluish-gray groundmass and coarse phenocrysts of quartz, feldspar, and hornblende. Near the contact with the country rock the phenocrysts are small and predominantly pink feldspar with an average length of about 2 mm. Towards the center of the intrusion the feldspar phenocrysts are larger and are associated with tabular quartz crystals which show a tendency toward a parallel vertical orientation, indicative of upward movement (Fig. 1). No attempt has been made to map the intrusive body or plot flow structures shown by crystal orientation.

The groundmass, composed of micro-granular quartz and feldspar, with a few scattered opaque minerals, and some chlorite, constitutes approximately 60 per cent of the rock. Some of the feldspar, having an index of refraction lower than Canada balsam, appears to be orthoclase. Rare, euhedral crystals of apatite and zircon are scattered through the matrix.

\* Published by permission of the Director, U. S. Geological Survey. Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 288.



Phenocrysts of feldspar, hornblende, and quartz (described separately) constitute about 40 per cent of the rock. The euhedral pink feldspar crystals with a maximum observed length of approximately 12 mm. have a composition near  $Ab_{78}An_{22}$ , or oligoclase-andesine. The sharp crystal borders are somewhat blurred by a reaction which has produced a brownish aureole about the crystals. Euhedral hornblende phenocrysts with a maximum observed length of approximately 7 mm. have also been attacked and almost completely altered to biotite, with a rim of opaque minerals and calcite. A few euhedral sphene crystals have borders which are partly resorbed and altered.

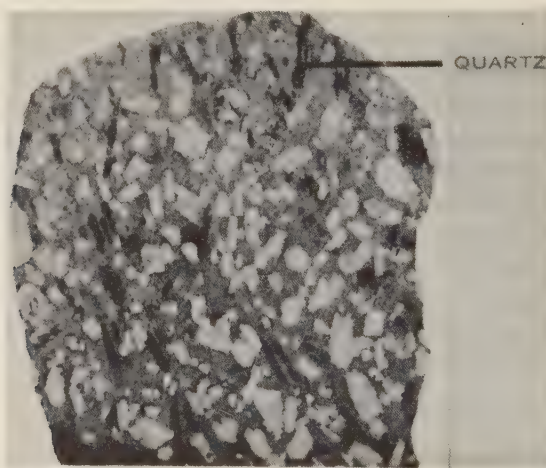


FIG. 1. Polished surface of quartz latite porphyry cut transverse to disc-like quartz phenocrysts (dark elongate areas). Note selective orientation of quartz and feldspar phenocrysts. Natural size.

#### QUARTZ PHENOCRYSTS

The tabular quartz phenocrysts are in large part concentrated in a zone intermediate between the contact of the intrusive with the country rock and the central part of the intrusive body. In the central mass the few crystals are generally unoriented and are not uniformly distributed. The phenocrysts occur as flattened and rounded discs (Figs. 1 and 2) with a maximum observed diameter of approximately 17 mm. and thickness of about 3 mm.; average diameter is somewhat less than 10 mm. All crystals lack measurable faces and edges because of strong resorption. At first they were believed to be quartz of unusual crystal form, showing either a remarkable development of basal or rhombohedral faces. However, their crystal habit and petrographic occurrence are such that the



FIG. 2. Quartz latite porphyry showing disc-like phenocrysts and molds from which they have weathered. Resorption patterns of quartz show in molds. Natural size.

crystals can only be attributed to the common tabular form of tridymite. X-ray powder patterns show that the phenocrysts are quartz.\* Each phenocryst is a single crystal and not an aggregate of quartz granules.

Numerous disc-like crystals were found weathered free from the matrix at the outcrop. Molds in the groundmass (Fig. 2) show definite patterns caused by the resorptive etching of the crystals. Similar patterns are easily visible on the crystals themselves and their development is well shown in thin section (Fig. 3).

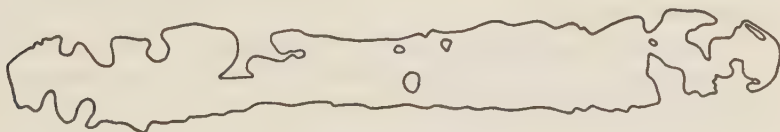


FIG. 3. Section through disc-like quartz phenocryst showing marked reentrants resulting from resorption.  $\times 10$ .

It was first assumed that the optic axis of the quartz would be normal to the basal faces of the tridymite crystals. Sections of fifteen crystals were cut as nearly parallel as possible (probably within a few degrees) to the basal faces and examined petrographically by means of the Fedorov stage to determine the position of the optic axis. Deviations of the optic

\* X-ray powder patterns by Mrs. Ursula Chaisson, Dept. of Mineralogy and Petrography, Harvard University.

axis from a direction normal to the basal face of the crystals varied from  $14^{\circ}$  to  $83^{\circ}$ , with an average of about  $61^{\circ}$ . Readings were:  $14^{\circ}$ ,  $52^{\circ}$ ,  $55^{\circ}$ ,  $56^{\circ}$ ,  $57^{\circ}$ ,  $60^{\circ}$ ,  $61^{\circ}$ ,  $62^{\circ}$ ,  $64^{\circ}$ ,  $65^{\circ}$ ,  $66^{\circ}$ ,  $67^{\circ}$ ,  $72^{\circ}$ ,  $78^{\circ}$ , and  $83^{\circ}$ .

These data show that a preferred orientation of the  $c$ -axis of quartz at an angle of  $61^{\circ} \pm 5^{\circ}$  to the  $c$ -axis of tridymite is highly probable. This might mean that the (10 $\bar{1}$ 1) face of tridymite has become the (0001) of quartz.

Quartz paramorphs after tridymite are not uncommon and have been previously described by Mallard (1) from the Euganean Hills of Italy and by Rogers (2) from California. None, however, has considered the crystallographic orientation of the quartz. Van Valkenburg and Buie (3) have pointed out that quartz paramorphs of octahedral cristobalite have a scattered orientation of the optic axis with respect to the octahedral axis.

Larsen (4) has pointed out that "should quartz be found that had crystallized from the magma as tridymite or cristobalite and inverted to quartz in the solid state, the crystallization from the magma might have taken place either above or below  $870^{\circ}$  C."\*\* Thus, the presence of tridymite phenocrysts does not necessarily indicate an unusually high temperature of crystallization. However, the large size of the phenocrysts in this rock suggests a leisurely crystallization under stable conditions rather than the hurried crystallization leading to most metastable forms. If this is true, the silica crystallized from this magma at temperatures above  $870^{\circ}$  C. At some stage the crystals were not in complete equilibrium with the fluid magma, as shown by their resorption.

Upward movement, shown by the orientation of the tabular phenocrysts, indicates considerable fluidity of the magma and a rapid chilling in the new environment.

It is suggested that detailed study of this interesting rock in both the field and laboratory may reveal considerable data on its paragenesis and the temperature of the magma.

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\*\* This temperature is for a pressure of one atmosphere, and will be higher for higher pressures.



# ANHYDRITE AND GYPSUM IN THE LYON MOUNTAIN MAGNETITE DEPOSIT OF THE NORTHEASTERN ADIRONDACKS

PAUL W. ZIMMER\*

## ABSTRACT

The occurrence of the minerals anhydrite and gypsum at the Chateaugay Mine at Lyon Mountain, New York is described. The anhydrite is believed to be hypogene and is compared with other previously described hypogene anhydrite deposits. The intergrowth of anhydrite and the magnetite in the absence of all sulfides suggests that the temperature range for anhydrite is greater than formerly believed. Gypsum is secondary in nature and derived from the anhydrite at this locality.

## INTRODUCTION

### *Location*

The Chateaugay Mine of the Republic Steel Corporation is located in the town of Lyon Mountain, Clinton County, New York. This is in the northwestern part of the Lyon Mountain Quadrangle at the north base of the mountain of the same name, one of the northernmost mountains of the Adirondack group.

### *Acknowledgments*

Thanks are due Mr. William J. Linney, District Manager, Chateaugay District, Republic Steel Corporation for making this study possible, and to Mr. Donald B. Gillies, Vice President of the corporation for permission to publish the paper. The writer is indebted to Dr. H. E. Culver, Dr. C. D. Campbell, and Dr. R. E. Wallace, of the State College of Washington, for critically reading the manuscript.

## GEOLOGY OF THE CHATEAUGAY MINE

The geology of the Chateaugay Mine area has been described by Miller.<sup>1</sup> The mine is located in the Lyon Mountain Granite at a place where the "gabbro phase" contaminates the granite. The area is considered by Gallagher<sup>2</sup> to be underlain in part at least by assimilated Grenville sediments. Magnetite occurs in two parallel zones designated as the footwall vein and hanging-wall vein. The magnetite has replaced pyroxene, albite, and microperthite, and in thin section commonly shows cata-

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<sup>1</sup> Miller, W. J., Geology of the Lyon Mountain Quadrangle, N. Y.: *N. Y. State Mus., Bull.* 271 (1926).

<sup>2</sup> Gallagher, David, Origin of the magnetite deposits at Lyon Mountain, N. Y.: *N. Y. State Mus., Bull.* 311 (1937).

clastic texture. These zones of magnetite parallel the strike, dip, and plunge of the mineral lineation as shown particularly by the pyroxene, through all the major and minor folds in the mine block. Throughout the mine and vicinity small amphibolite zones, locally called "Gray Bands," are distributed irregularly. About 500 feet from the footwall vein into the footwall, and a similar distance from the hanging-wall vein into the hanging wall, two thick amphibolite zones have been located. These "Gray Bands" and possibly the amphibolite zones may be remnants of the old Grenville sediments partly assimilated.



FIG. 1. Drawing of thin section from the 1813 level in the hanging-wall ore zone, showing magnetite (black) rim around micropertthite (mp) with tongues into the anhydrite (an) as well as along the crystal boundaries. Aegirinaugite (ae).



FIG. 2. Drawing of thin section from the 2113 level in the footwall ore zone, showing magnetite (black) in the crushed anhydrite (can) zone as well as a tongue into the anhydrite (an) crystal. Aegirinaugite (ae)

#### ANDHYDRITE

On the 1813 level (El. 350', about 1600' below shaft collar) a raise penetrated a large body of magnetite intergrown with anhydrite, and aegirinaugite. This was in the hanging-wall vein; a similar body has been found in the footwall vein on the 2113 level (El. 50'). Anhydrite has also been found within 300 feet of the surface, both as a vein cross-cutting the magnetite body, and as a mutual intergrowth with the magnetite.

The association of the anhydrite and magnetite as seen in Fig. 1 in which magnetite appears to be replacing anhydrite along the crystal boundaries as well as in several tongues into the anhydrite crystals, suggests that anhydrite in this section was earlier than magnetite. In Fig. 2. early anhydrite is highly crushed and magnetite was introduced within

this crush zone with a tongue into the solid anhydrite crystal. The drawing in Fig. 3 shows a vein of anhydrite cross cutting the magnetite ore zone, definitely showing the late nature of this anhydrite.

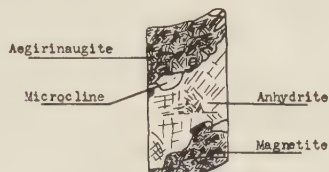


FIG. 3. Drawing of diamond drill core showing anhydrite vein cutting across the magnetite ore zone 297' from surface.  
( $\frac{1}{2}$  natural size)

From the results of the work by Newhouse<sup>3</sup> in which he states that "... the mutual-boundary relation can have no particular significance in interpretation of mineral relations," seemingly unwarranted importance is placed on the interpretation of the mutual boundary between anhydrite and magnetite, a relationship that is commonly seen. With the definite proof that part of the anhydrite is earlier than, and part is later than, the magnetite, I feel that the mutual boundary is here strongly indicative of simultaneous deposition.

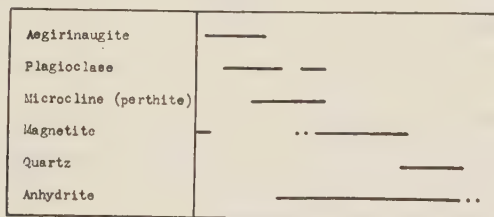


FIG. 4. Diagram showing the age relations of the principal minerals in the ore zone at Lyon Mountain, N. Y.

The diagram in Fig. 4 shows age relations of the anhydrite as seen in the thin sections. This occurrence of anhydrite in the magnetite zone at Lyon Mountain, which Gallagher<sup>4</sup> considers the result of pneumatolytic metasomatism, suggests a high upper limit to the temperature range for the formation of anhydrite.

Optically this anhydrite shows normal characteristics ( $\alpha=1.570$ ,  $\beta=1.575$ ,  $\gamma=1.615$ ,  $2V=45^\circ \pm$ ). The cleavage at right angles and the

<sup>3</sup> Newhouse (1928), The microscopic criteria of replacement. Chapt. VIII p. 160, Laboratory Investigation of the Ores., McGraw-Hill, N. Y.; Fairbanks editor.

<sup>4</sup> Gallagher, David (1937), *op. cit.*, p. 79.



twinning show up in both the thin section and the powder. X-ray powder diffraction pattern shows a marked degree of similarity with a sample of anhydrite from Hillsboro, New Brunswick. Similarly, the calculated  $d$  spacings have been compared with the  $d$  spacings of anhydrite as recorded in the American Society for X-ray and Electron Diffraction card index. In both cases there were six extra lines on the Lyon Mountain anhydrite that suggests either impurities or a slightly different form. Checking the card index against these lines for minerals that were known to be in the area did not show any similarity. This suggests a deviation in form from the previously measured anhydrite.

This mode of occurrence is in contrast with that of previously described hypogene anhydrite. Butler<sup>5</sup> in a paper in 1919 records and describes localities known at that time. The nature of occurrence of anhydrite in seven more localities are described below in order to bring this list up to date.

Anhydrite has been described in the Ajo Mining District in Arizona by Gilluly<sup>6</sup> at such depths below the supergene zone, and associated with such minerals as pyrite, chalcopyrite, and barite, as to suggest its hypogene origin.

Langford and Hancox<sup>7</sup> describe hypogene anhydrite at the McIntyre Mine in Ontario, Canada, where it is found at depths of 2000 to 4000 feet and associated with the ore minerals galena, sphalerite, chalcopyrite, and pyrite. Brown<sup>8</sup> describes anhydrite in the zinc mines at Balmat, N. Y., with sphalerite, galena, chalcopyrite, pyrrhotite, and pyrite in metamorphosed Grenville sediments.

Osborn<sup>9</sup> has described another deposit of anhydrite in the Grenville metamorphic sediments from the Calumet Mine, Calumet Island, Quebec, Canada. There the anhydrite is replacing the deformed limestone. Osborn also describes two other occurrences of anhydrite, one, the Bonne-camp map area, within the Grenville, and the other within the alkaline gabbro of Mount Royal. This latter was described as being pyrogenetic by Bancroft and Howard.<sup>10</sup>

In all of these localities anhydrite is associated with sulfide minerals.

<sup>5</sup> Butler, B. S., Primary hypogene sulfate minerals in ore deposits: *Econ. Geol.*, **14**, 581-609 (1919).

<sup>6</sup> Gilluly, J., The Ajo Mining District, Arizona: *U.S.G.S. Prof. Paper* 209 (1946).

<sup>7</sup> Langford, G. B., and Hancox, E. G., Hypogene anhydrite from McIntyre Mine. Porcupine District, Ontario: *Econ. Geol.*, **31**, 600-609 (1936).

<sup>8</sup> Brown, J. S., Structure and primary mineralization of the zinc mine at Balmat, N. Y.: *Econ. Geol.*, **31**, 233-258 (1936).

<sup>9</sup> Osborn, F. F., Anhydrite and gypsum at Calumet Mine, Calumet Island, Quebec: *Contrib. Can. Min.*, U. of Toronto Studies, No. **46** (1941).

<sup>10</sup> Bancroft, J. A., and Howard, W. V., The essexites of Mount Royal, Montreal, P. Q.: *Trans. Roy. Soc. Can.*, **17**, sec. 4, 13-43 (1923).

In contrast to this, at Lyon Mountain essentially no sulfides have been found. The occurrence of anhydrite at Britannia Beach, B. C., in a vein system separate from the sulfide mineralization as described by James<sup>11</sup> is of interest here. Although he believes the anhydrite to be primary but younger than the copper mineralization, it is important to record this deposition of sulfates without sulfides.

The relative insolubility of anhydrite at high temperatures<sup>12</sup> led Lindgren<sup>13</sup> and Butler<sup>14</sup> to conclude that calcium sulfate was not in the ascending solutions as such at high temperatures, but that the sulfur trioxide was in the ascending solutions, and when it came in contact with the calcium in descending solutions, the anhydrite was deposited at relatively high temperatures as hypogene deposits. Butler<sup>15</sup> later describes two possible methods for the formation of sulfates from igneous emanations: (1) In the presence of free oxygen and sulfur or sulfur dioxide, as they cool sulfur trioxide would form and at suitable temperatures the sulfates would form. At the time of Butler's paper all the deposits of anhydrite were associated with sulfides and this method would necessitate the supposition that sulfides and sulfates were deposited in the presence of free oxygen, which is not likely. (2) If emanations contain no free oxygen the oxides of metals formed at high temperatures may be reduced at lower temperatures to form oxides of sulfur. The dissociation of sulfur trioxide at 450° C. is cited by Butler as the limiting temperature for the formation of sulfates and suggests that because the boiling temperature of H<sub>2</sub>SO<sub>4</sub> is much lower probably they would form at much lower temperatures. Sulfates probably will not form above 200° C.

Above 450° C. sulfur trioxide is in equilibrium with sulfur dioxide and oxygen in amounts shown by the curves in Butler's paper. As he points out the amount of sulfur trioxide would be small and become less the higher the temperature. If conditions were such that the small amount of sulfur trioxide would react with calcium present to form anhydrite, which is very insoluble at these high temperatures, the sulfur trioxide would be removed from the system. The equilibrium of the system would thus be lost and the formation of sulfur trioxide would be favored to regain this lost equilibrium. It seems that the temperature above which sulfur trioxide is all decomposed (1000° C.) is the maximum temperature for the formation of anhydrite. This is well above the temperature of hypogene mineralization.

<sup>11</sup> James, H. T., Britannia Beach map area, B. C.: *Geol. Surv. Can., Mem.* **158** (1929).

<sup>12</sup> Posnjak, E., The system CaSO<sub>4</sub>-H<sub>2</sub>O: *Am. Jour. Sci.* (V) **35A**, 247-272 (1938).

<sup>13</sup> Lindgren, W. T., Anhydrite as a gangue mineral: *Econ. Geol.*, **5**, 422-527 (1912).

<sup>14</sup> Butler, B. S., Geology and ore deposits of San Francisco and adjacent districts, Utah: *U.S.G.S., Prof. Paper* **80** (1913).

<sup>15</sup> Butler, B. S. (1919), *op. cit.*, p. 609.

Butler<sup>16</sup> has described how the wall-rock alteration in the Cactus Mine might supply the necessary calcium for the formation of anhydrite. At Ajo the calcium for the anhydrite possibly was derived from the wall-rock alterations also, as Gilluly<sup>17</sup> describes albitization at this locality with the removal of the calcium from the rock. At both of these localities the wall rock is monzonite which generally contains an adequate supply of calcium.

At Lyon Mountain the low percentage of calcium in the wall rocks, which are granites and syenites, is noteworthy because such a low amount of calcium would not make this a very likely source rock for the calcium necessary for the formation of anhydrite. Buddington's<sup>18</sup> average of five Alexander type granites in the Adirondacks gives 0.86% CaO. Recent analyses of syenites at Lyon Mountain give 2.01% CaO.<sup>19</sup> These may be contrasted with the average that Daly<sup>20</sup> gives of 12 monzonites, 6.5% CaO.

Early carbonates in the McIntyre Mine are described by Langford and Hancox<sup>21</sup> as the source for the calcium there. Carbonates do not occur in the ore at Lyon Mountain except as much later veins.

The presence of anhydrite in the Grenville sediments at Balmat, Calumet, and also at the Bonnescamp map area suggests that these sediments were the source for the calcium, and as pointed out by Brown<sup>22</sup> might be the source for the sulfates. The small amount of "Gray Band" which has been considered to be assimilated Grenville sediments has from 9 to 12% CaO, and possibly may be the source of the calcium at Lyon Mountain.

#### GYP SUM

Selenite is not uncommon in the shaft between the 1513 level (El. 600') and the 2113 level (El. 50') and generally is found intergrown with aegirinaugite, magnetite, microcline, sphene, and quartz in cavities similar to those described by Gallagher<sup>23</sup> as miarolitic gas cavities. At the time of Gallagher's work the mine had not been developed below the 1513 level.

<sup>16</sup> Butler, B. S. (1913), *op. cit.*, p. 124.

<sup>17</sup> Gilluly, J. (1946), *op. cit.*

<sup>18</sup> Buddington, A. F., Adirondack Igneous Rocks and their Metamorphism: *G.S.A.*, Mem. 7, 148 (1933).

<sup>19</sup> Average of eight samples of syenite. Analyst Waltz, chief chemist, Republic Steel Corporation, Canton, Ohio.

<sup>20</sup> Daly, R.A., Igneous Rocks and the Depths of the Earth, McGraw-Hill, N. Y., 9-13 (1933).

<sup>21</sup> Langford, G. B., and Hancox, E. G., *op. cit.*, p. 604.

<sup>22</sup> Brown, J. S., Natural gas, salt, and gypsum in pre-Cambrian rocks at Edwards, N. Y.: *Bull. Am. Ass. Petro. Geol.*, **16**, 727-735 (1932).

<sup>23</sup> Gallagher, David, (1937), *op. cit.*, p. 17.

A large cavity which contained a single swallowtail selenite twin 32 inches long was found a few hundred feet from the shaft toward the hanging-wall ore zone on the 1813 level (El. 350'). One end of the crystal was intergrown with microcline, quartz, aegirinaugite, and magnetite crystals of the cavity lining. Gallagher<sup>24</sup> has suggested that these cavities in the syenite are of primary origin. If this were true, the selenite should be considered primary. However, one wall of the cavity is a diabase dike covered with calcite and small albite crystals. Obviously, the opening could not have existed at the time of the dike invasion without being filled with the diabasic magma, so that the idea that the cavities are secondary as suggested by Whitlock<sup>25</sup> is strongly supported. There have been five of these cavities with similar dike relationships found to date.

Commonly these cavities are found full of water confined under considerable pressure. Prider's<sup>26</sup> suggestion that the formation of gypsum crystals in cavities is due to a decrease in pressure accompanied by evaporation, may account for selenite crystals at the Chateaugay Mine.

In the lower levels of the mine the horizontal joints are frequently found coated with gypsum and/or calcite. In the upper levels the surface waters have washed the joints clean of all secondary minerals. Although Whitlock examined the locality in 1905 before the present mine was opened and at a time when there was no development below the 800 level, he does describe a type of calcite crystal which is characteristic of deposition from corrosive waters frequently associated with gypsum.<sup>27</sup> This deposition with secondary calcite further suggests the secondary nature of the gypsum.

The anhydrite was probably the source of the gypsum for the anhydrite in several sections shows this alteration in progress along the cleavage of the anhydrite.

#### CONCLUSIONS

At Lyon Mountain all of the anhydrite found has been in the magnetite zones. The continuous deposition of the anhydrite previous to, simultaneous with, and continuing beyond the deposition of the magnetite suggests that the anhydrite is a mineral of the hypothermal temperature range at this locality. The "Gray Band," which is considered to be assimilated Grenville sediments, is the only known source for the calcium which is needed to form the anhydrite.

The gypsum is secondary in nature and derived from the anhydrite.

<sup>24</sup> Gallagher, David, (1937), *op. cit.*, p. 19-21.

<sup>25</sup> Whitlock, H. P., Minerals from Lyon Mountain, Clinton County: *N. Y. State Mus., Bull.* 107, 55-96 (1907).

<sup>26</sup> Prider, R. T., An unusual occurrence of gypsum at Kalgoorlie, Western Australia: *Am. Mineral.*, 25, 591-605 (1940).

<sup>27</sup> Whitlock, H. P. (1907), *op. cit.*, p. 63.



# GROUTITE, $\text{HMnO}_2$ , A NEW MINERAL OF THE DIASPORE-GOETHITE GROUP

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## ABSTRACT

Groutite,  $\text{HMnO}_2$  is a new member of the diaspore-goethite group. It resembles manganite in general appearance as in luster, color, streak, hardness and specific gravity. Its structure, crystal forms and habits, cleavage and pleochroism are different. It occurs on the Cuyuna range, Minnesota, associated with iron ores.

## INTRODUCTION

In 1942 the writer was presented with a small group of beautiful black crystals of a manganese mineral which had been thought to be manganite. The crystal habit of the mineral was so different, however, that an  $x$ -ray powder diagram was prepared which gave a pattern entirely different from any other known manganese mineral. A search for more material revealed that the mineral is not rare in the iron mines of the Cuyuna range of Minnesota. Some very fine specimens were presented to the writer by Mr. George Chamberlin, chief mining engineer of Pickands, Mather and Company at Crosby, Minn. The original sample examined was obtained from Mr. Harvey J. Hakala, mining engineer of the Oliver Iron Mining Company. It came from the Sagamore open pit west of Ironton on the Cuyuna range. Dr. R. B. Ellestad made the analysis. To all these men the writer is greatly indebted. Grants by the Graduate School of the University of Minnesota are gratefully acknowledged.

## CRYSTALLOGRAPHY

Very beautiful specimens of hundreds of crystals, up to 5 mm. in greatest dimensions were available. Examination shows that the vast majority of the crystals are wedge or lens-shaped and that their faces are rounded and curved in a way that makes their measurements almost impossible. They have many markings on them similar to those of Fig. 3 which represents a sketch of what is visible of most crystals. The vertical  $[001]$  zone is always striated parallel to the  $c$  axis. The only usable vertical forms were  $\{110\}$  and  $\{120\}$ , and measurements on them are accurate to only the nearest degree. Form  $\{010\}$  occurs as very narrow faces but the brachypinacoidal cleavage is so perfect that reflections from it were very valuable. Another form in the vertical zone, probably present, is  $\{130\}$ . Form  $\{100\}$  was not observed but cleavage parallel to it may be seen, though interrupted by the perfect cleaving parallel to  $\{010\}$ . The read-

ings on the forms  $\{111\}$  and  $\{021\}$  are usually fair and accurate to the nearest 10 minutes, though they are commonly smaller than shown in Fig. 2. Form (134) was observed only twice, and then only as one face on a crystal. It was large and gave good signals. Vicinal and curved faces precluded any other measurements. The crystals are attached to the walls of the cavities with the plane of the  $a$  and  $b$  axes more or less normal to their supports. This occurrence emphasizes their wedge- and lens-like shapes.

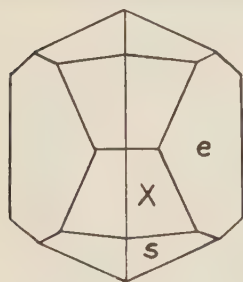


FIG. 1



FIG. 2



FIG. 3

In recording the crystal elements and forms, the new edition of the *System of Mineralogy* (1) has been followed. All angles and other calculations are based on the reliable  $x$ -ray data below. If only two circle goniometric values had been used, the axial ratio would have been 0.440:1:0.268.

## ELEMENTS

Orthorhombic dipyramidal class

$$a:b:c = 0.4262:1:0.2663$$

$$p_0:q_0:r_0 = 0.6248:0.2663:1$$

$$q_1:r_1:p_1 = 0.4262:1.6004:1$$

$$r_2:p_2:q_2 = 3.7550:2.3463:1$$

TABLE 1. FORMS OBSERVED

| Form | Indices | $\phi$ | $\rho$ | $\phi_1$ | $\rho_1$ | $\phi_2$ | $\rho_2$ |
|------|---------|--------|--------|----------|----------|----------|----------|
| $b$  | 010     | 0°00'  | 90°00' | 90°00'   | 90°00'   | — —      | 0°00'    |
| $m$  | 110     | 66 55  | 90 00  | 90 00    | 23 05    | 0°00'    | 66 55    |
| $y$  | 120     | 49 33  | 90 00  | 90 00    | 40 27    | 0 00     | 49 33    |
| $e$  | 021     | 0 00   | 28 02  | 28 02    | 90 00    | 90 00    | 61 58    |
| $s$  | 111     | 66 55  | 34 12  | 14 55    | 58 53    | 58 00    | 77 16    |
| $x$  | 134     | 38 02  | 14 14  | 11 18    | 81 17    | 81 07    | 78 50    |

## STRUCTURAL DATA

Powder and rotation photographs about the  $[100]$  and  $[001]$  directions were made. It is planned to make a complete determination of the struc-

ture at some later date. There is such similarity in the data of groutite, diaspore and particularly goethite, however, that the new mineral must be isostructural with the other two. The size of the unit cell is  $a_0 = 4.56 \text{ \AA}$ ,  $b_0 = 10.70 \text{ \AA}$ ,  $c_0 = 2.85 \text{ \AA}$ . It is interesting to observe that the height of the unit cell is  $2.85 \text{ \AA}$ , or possibly twice this value, which is the same as

TABLE 2. POWDER PHOTOGRAPH OF GROUTITE, SAGAMORE MINE, NEAR IRONTON, MINN.  
Unfiltered Fe radiation. Radius of camera 57.3 mm. Indices obtained  
from rotation photographs.

| No. of line | $d$   | $I$ | Indices | No. of line | $d$   | $I$  | Indices  |
|-------------|-------|-----|---------|-------------|-------|------|----------|
| 1           | 5.36  | 1   | 020     | 19          | 1.465 | 1    |          |
| 2           | 4.17  | 10+ | 110     | 20          | 1.448 | 1    |          |
| 3           | 3.462 | 1-2 | 120     | 21          | 1.435 | 2    |          |
| 4           | 2.798 | 6   | 130     | 22          | 1.398 | 1    |          |
| 5           | 2.675 | 6   | 040     | 23          | 1.367 | .5-1 |          |
| 6           | 2.524 | 1   | 021     | 24          | 1.345 | 1    |          |
| 7           | 2.369 | 6   |         | 25          | 1.304 | .5   |          |
| 8           | 2.303 | 5   | 140     | 26          | 1.286 | 1    | }180?    |
| 9           | 2.210 | 2   |         | 27          | 1.281 | 1    |          |
| 10          | 2.008 | 1   |         | 28          | 1.267 | 1    |          |
| 10a         | 1.959 | .5  | 041     | 29          | 1.258 | 1    |          |
| 11          | 1.932 | 1   | 150     | 30          | 1.220 | 1    |          |
| 12          | 1.798 | .5  |         | 31          | 1.212 | 1    | 081      |
| 13          | 1.763 | 2   |         | 32          | 1.202 | 1    |          |
| 14          | 1.732 | 1   |         | 33          | 1.153 | 2    |          |
| 15          | 1.692 | 5   |         | 34          | 1.134 | 1-2  |          |
| 16          | 1.603 | 4   |         | 35          | 1.107 | 1    |          |
| 17          | 1.559 | 0   |         | 36          | 1.086 | .5   |          |
| 18          | 1.515 | 3   | 061     | 37          | 1.077 | .5   |          |
|             |       |     |         | 38          | 1.068 | 3    | 0, 10, 0 |

that of pyrolusite, Ba-psilomelane, cryptomelane and manganite (in the latter  $5.70/2$ ). While those minerals have habits of elongation parallel to  $[001]$ , groutite crystals are very short in this direction. The lines of the powder photograph are included here (Table 2) because in very fine grained specimens it might be impossible to distinguish groutite from manganite by any other means.

#### PHYSICAL PROPERTIES

Cleavage occurs parallel to  $\{010\}$  and  $\{100\}$ . The former is exceedingly perfect and yields brilliant reflections. The color of the mineral is jet black, and the luster is brilliant submetallic to adamantine. The streak is dark brown like that of manganite. The hardness may be slightly less than that of manganite, the brittleness seems to be the same. The specific

gravity determined on a gram of handpicked material is 4.144 recalculated to 4° C. This determination was made in a fused silica pycnometer. The theoretical density based on the size of the unit cell is 4.172. The optical properties have not been determined except for pleochroism, which is very strong in white light.

TABLE 3. CHEMICAL ANALYSES

|                                | 1        | 1<br>minus<br>residue | 2     | Theoretical<br>composition |
|--------------------------------|----------|-----------------------|-------|----------------------------|
| MnO                            | 78.06    | 79.97                 | 80.04 | 80.66                      |
| O                              | 8.73     | 8.94                  | 9.02  | 9.10                       |
| H <sub>2</sub> O+              | 10.14    | 10.39                 |       | 10.24                      |
| H <sub>2</sub> O—              | .04      | .04                   |       |                            |
| Al <sub>2</sub> O <sub>3</sub> | not det. |                       |       |                            |
| Fe <sub>2</sub> O <sub>3</sub> | .02      | .02                   |       |                            |
| (Na,K) <sub>2</sub> O          | not det. |                       |       |                            |
| BaO                            | .00      |                       |       |                            |
| P <sub>2</sub> O <sub>5</sub>  | .33      | .34                   | .07   |                            |
| Insoluble residue              | 2.39     |                       |       |                            |
| Total                          | 99.70    | 99.71                 |       | 100.00                     |

R. B. ELLESTAD, *analyst*.

Very dark brown to black [001]  
Yellowish brown [010]

Groutite could be distinguished from manganite by this property since the pleochroism of this mineral is weak.

Groutite is infusible and loses water on heating in air at temperatures above 200° C. Heating at 150° C. in air for five days does not affect it.

#### CHEMICAL COMPOSITION

Material for the analyses was handpicked very carefully. Analysis 1 is from a specimen from the Mahnomen Mine, according to Mr. George Chamberlin who presented it to the writer. The associated quartz could not be eliminated completely and is recorded as insoluble. Partial analysis 2 is on a sample from the Sagamore Mine, which contains no insoluble residue. Dr. R. B. Ellestad kindly furnished the note\* below regarding

\* Total manganese was determined by potentiometric titration of manganous ion with permanganate, in a neutral pyrophosphate solution, following the method of Lingane and Karplus (*Ind. and Eng. Chem., Analytical Ed.* **18**, 191, 1946). Excess oxygen was determined by solution of the sample in a mixture of sulfuric acid and an excess of standard sodium arsenite, followed by the titration of the excess arsenite with permanganate. This method is described by Kolthoff and Sandell (*Textbook of Quantitative Inorganic Analysis*,



analytical procedure. Dr. W. W. Wetzel of Minnesota Mining and Manufacturing Company, St. Paul, Minn., kindly ran a spectrographic analysis for the writer. He reports less than 0.1% CaO, about 0.05 MgO, about 0.05 Na<sub>2</sub>O and a trace of Al<sub>2</sub>O<sub>3</sub>.<sup>1</sup>

#### OCCURRENCE

Groutite, as stated in the introduction, has been found in at least three mines of the Cuyuna iron range in Minnesota. There is good reason to believe that it is present as minute crystals in other mines of the district. Very fine specimens have been obtained from the Sagamore, Mangan No. 2, and Mahnomen pits. Since these specimens are very attractive even to the layman, it is probable that a number of them, if not many, are in local collections. The crystals always line vugs and nearly always are associated with manganite. The manganite usually is the common variety which forms radiating columnar but compact coatings, occasionally one inch thick. The groutite crystals are attached to the tops of the columns approximately with their (100) planes. In at least one specimen the manganite columns are elongated parallel to the [100] direction, and the attached groutite crystals have their [100] parallel to that of the manganite. Some crystals seem to show oriented growth on the manganite with the plane (100) in common. Since the  $c_0$  and  $b_0$  dimensions are very similar this is not surprising.

In one specimen unusual manganite crystals were observed which may correspond to one of several varieties described by Flink (3). They are very thin and platy in habit and have the shape of the end of a gladiator's sword. The very thin terminal faces are somewhat rounded. Deep striations parallel to the elongation prevent measuring of any faces in the vertical zone.

The only other minerals associated with groutite are colorless quartz crystals, hematite and goethite. A thin coating of calcite may be found on some specimens. These can be dissolved with dilute H<sub>2</sub>SO<sub>4</sub> without harming the manganese minerals.

#### RELATIONSHIP TO DIASPORE AND GOETHITE

Until recent years it had been thought that manganite was a member of the diaspore-goethite group. M. J. Buerger (2) has shown, however, that the bonding of hydrogen corresponds more closely to an OH ion in

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p. 605; Macmillan, N. Y., 1943). Total water was determined by the Penfield method, using a flux of lead oxide.

<sup>1</sup> A spectrographic analysis was made by Dr. H. C. Harrison in Professor Esper Larsen's laboratory. It was received too late for inclusion above. He reports concentrations 0.1–0.01% of Al, Fe, Mg, Ca, Zr, Mo, Sb, Sn. Concentrations 0.01–0.001% of Na, K, Ti, Ni, Hf, Pb, Y, Gd, Sc, Yb, Cr, V, Cu, Ag, Ba, Li, Sr, Bi.

manganite. Similar bonds exist in boehmite and lepidocrocite. These three minerals can be placed in one group, therefore, though it must be admitted that manganite is not too closely related. It might conceivably be placed between the two groups because the dimensions of its unit cell are close to those of groutite as shown in Table 4.

TABLE 4. COMPARISON OF UNIT CELLS, VOLUMES, AND AXIAL RATIOS

|               | $a_0$ | $b_0$ | $c_0$ | Volume | Axial ratios   |
|---------------|-------|-------|-------|--------|----------------|
| diaspore      | 4.40  | 9.39  | 2.84  | 117.34 | .4689:1: .3019 |
| goethite      | 4.64  | 10.00 | 3.03  | 140.59 | .4593:1: .3034 |
| groutite      | 4.56  | 10.70 | 2.85  | 139.05 | .4262:1: .2663 |
| manganite     | 8.86  | 5.24  | 5.70  | —      |                |
| manganite*    | 4.43  | 10.48 | 2.85  | 132.33 | .4227:1: .2719 |
| boehmite      | 3.78  | 11.08 | 2.85  | 119.36 | .320:1: .242   |
| lepidocrocite | 3.87  | 12.51 | 3.06  | 148.13 | .309:1: .245   |

\* The dimensions have been divided or multiplied, respectively, by 2 to conform to other minerals in the table.

The volumes of unit cells containing the same number of chemical molecules are shown in Table 4. The smaller ones would be expected to belong to the minerals with the greater stability. Diaspore and boehmite are similar in stability. Lepidocrocite is considerably larger in volume than goethite and less stable under pressure and elevated temperatures.† For this reason it is also a rare mineral. The same applies to the manganese dimorphs. Groutite probably forms only under unusual conditions as evidenced by its limited occurrence and association.

### CONCLUSION

A new manganese oxide monohydrate has been discovered on the Cuyuna range in Minnesota. It has been named groutite for Professor F. F. Grout of the University of Minnesota. The mineral is a member of the diaspore-goethite group and has the formula  $\text{HMnO}_2$ . It forms orthorhombic, black, wedge-shaped crystals with a high submetallic luster. Its streak is dark brown, and it exhibits strong pleochroism. Specific gravity 4.14. The mineral has a highly perfect cleavage parallel (010) and less so parallel (100). Its unit cell dimensions are:  $a_0$  4.56,  $b_0$  10.70,  $c_0$  2.85 Å.

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† According to unpublished recent experiments by the writer.

## BEYERITE FROM COLORADO\*

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### ABSTRACT

Bismutite is a common accessory mineral in pegmatites in Colorado and northern New Mexico. In three pegmatites in south-central Colorado (Mica Lode and School Section deposits, Fremont County, and Meyers Ranch body, Park County) beyerite is intergrown with bismutite. These minerals are supergene alterations of late, hydrothermal, metallic minerals—native bismuth, bismuthinite, and various bismuth-bearing sulfosalts. Beyerite, which is analyzed for the first time, has the composition  $(\text{Ca, Pb}) \text{Bi}_2 (\text{CO}_3)_2 \text{O}_2$ , two molecules of which are contained in the unit cell.

### INTRODUCTION

During the fall of 1942 and the spring of 1943 the writer examined pegmatite deposits in south-central Colorado for the Geological Survey, United States Department of the Interior. During these investigations bismuth carbonates were observed as accessory pegmatite minerals. A preliminary note on their occurrence has been recorded (Heinrich, 1946). Field work on Colorado pegmatites was resumed in the summer of 1946 under a grant from the Brodrick Fund of Harvard University. The work centered around the Eight Mile Park area, just west of Canon City (Heinrich, 1947, and Wolfe and Heinrich, 1947) but other pegmatite districts in Colorado also were examined. The occurrence of bismuth minerals in the pegmatites was studied in detail. The purpose of this paper is to describe the geology and mineralogy of the rare mineral beyerite and to record the pegmatite occurrences of bismuth carbonate minerals.

The writer is indebted to the members of the Department of Mineralogy and Petrography of Harvard University for considerable advice and assistance. Professor E. S. Larsen read much of the manuscript in thesis form. Professor Clifford Frondel guided the laboratory study of beyerite and Professor C. S. Hurlbut, Jr., completed a critical reading of this manuscript. The writer also wishes to thank Dr. John C. Rabbitt of the U. S. Geological Survey for the spectrographic analyses, Mr. F. A. Gonyer of the Department of Mineralogy and Petrography, Harvard University, for his careful and patient work in the beyerite analyses, particularly in the lead determinations, and Dr. C. Wroe Wolfe of Boston University for assistance in several details of laboratory procedure. The cost of the analyses was met by the Department of Mineralogy and Petrography.

\* Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 289.

## BISMUTH CARBONATE MINERALS IN PEGMATITES

Bismuth carbonates, chiefly as bismutite, appear to be widespread supergene accessory minerals in pegmatites. Frondel (1943, pp. 529 and 532) lists pegmatite localities in New Mexico (Petaca District), North Carolina (Cashiers Valley District), Colorado (Salida region), Connecticut (Hales Quarry, Portland), California (Pala), and Arizona (pegmatite?). Jahns (1946*A*, pp. 67–68 and 1946*B*), who has described the occurrence of bismutite in the pegmatites of the Petaca district, New Mexico, reports that it has been found in 48 deposits there and in a number of pegmatites in the nearby Ojo Caliente district. A detailed description of the mineralogy of the Petaca deposits is in progress (Heinrich and Jahns, 1947). Bismutite also occurs as a common accessory mineral in the Harding pegmatite, Taos County, New Mexico, where it forms as an alteration of native bismuth.<sup>1</sup> According to Jahns,<sup>2</sup> “. . . both bismutite and native bismuth occur in several pegmatites in the general Sangre de Cristo area. Rather impressive quantities fill fractures in parts of the Rociada lepidolite occurrence . . .” A brief note on these occurrences has been published (Jahns, 1946*C*).

Some pegmatites contain both bright yellow and bright green bismutite. Spectrographic analyses show that the green varieties contain a higher percentage of copper as an impurity:

|                              | % CuO in bright<br>yellow bismutite | % CuO in bright<br>green bismutite |
|------------------------------|-------------------------------------|------------------------------------|
| Harding pegmatite, N. M.     | .05%                                | >1.0%                              |
| Devils Hole pegmatite, Colo. | 0.2%                                | 0.5%                               |

Table 1 summarizes the occurrences of bismuth carbonate minerals in Colorado pegmatites. In all of these deposits the carbonates are clearly secondary minerals formed by the alteration of native bismuth, bismuth sulfide, or a bismuth-bearing sulfosalt. Although details regarding the conditions of formation of the original bismuth minerals are generally absent, the mineral association and manner of occurrence of the alteration products (generally as fracture fillings) serve to indicate that the original materials were late hydrothermal pegmatite minerals.

## PREVIOUS WORK ON BEYERITE

The name, *beyerite*, was applied by Frondel (1943, p. 532) to a new species of bismuth carbonate, “. . . first found as pulverulent earthy

<sup>1</sup> Checked by x-ray powder photographs, by the writer.

<sup>2</sup> Jahns, Richard H., private communication, 1947.



TABLE 1. OCCURRENCES OF BISMUTH CARBONATE MINERALS IN COLORADO PEGMATITES

| Deposit                                                   | Mineral*                      | Color                        | Texture                          | Host Mineral | Associated Minerals                                                            | Original Mineral                                                           |
|-----------------------------------------------------------|-------------------------------|------------------------------|----------------------------------|--------------|--------------------------------------------------------------------------------|----------------------------------------------------------------------------|
| 1. Wood Gulch pegmatite, Gunnison Co.                     | bismutite                     | bright yellow, greenish-gray | earthy                           | quartz       | albite, muscovite, columbite, garnet                                           | ?                                                                          |
| 2. Yard pegmatite, Trout Creek Pass, Chaffee Co.          | bismutite                     | gray, brown, green           | earthy                           | quartz       | monazite, euxenite, fluorite, albite, malachite                                | probably a copper-bismuth sulfosalt                                        |
| 3. Meyers Ranch pegmatite, Park Co.                       | (a) bismutite<br>(b) beyerite | yellow, brown                | earthy<br>waxy                   | quartz       | albite, beryl, muscovite                                                       | ?                                                                          |
| 4. Rosemont pegmatite, Micanite, Park Co.                 | bismutite                     | white, gray, green           | earthy                           | quartz       | muscovite, albite, garnet, malachite                                           | possibly a copper-bismuth sulfosalt                                        |
| 5. Devils Hole pegmatite, Fremont Co.                     | bismutite                     | yellow, green, gray, black   | waxy, and as minute green fibers | quartz       | albite, muscovite                                                              | possibly a copper-bismuth sulfosalt and needle-like form indicate cosalite |
| 6. School Section pegmatite, Eight Mile Park, Fremont Co. | (a) bismutite<br>(b) beyerite | gray                         | earthy                           | albite       | albite, muscovite, black tourmaline, chalcocite, malachite, native silver (tr) | probably a copper-bismuth sulfosalt                                        |
| 7. Mica Lode pegmatite, Eight Mile Park, Fremont Co.      | (a) bismutite<br>(b) beyerite | gray                         | earthy                           | muscovite    | albite, muscovite, chalcocite, native bismuth (tr), malachite                  | probably a copper-bismuth sulfosalt                                        |
| 8. Meyers Quarry, Eight Mile Park, Fremont Co.            | bismutite                     | yellow, green, gray          | earthy                           | microcline   | albite, muscovite, malachite                                                   | possibly a copper-bismuth sulfosalt                                        |
| 9. Border Feldspar No. 1, Eight Mile Park, Fremont Co.    | bismutite                     | gray                         | earthy                           | albite       | muscovite, beryl, black tourmaline, sericite                                   | ?                                                                          |
| 10. Burroughs pegmatite, Jefferson Co.                    | bismutite                     | gray, green                  | earthy, as rods                  | quartz       | malachite                                                                      | probably aikinite                                                          |
| 11. Bigger pegmatite, Jefferson Co.                       | bismutite                     | yellow                       | earthy                           | quartz       | albite, muscovite, beryl                                                       | probably bismuthinite                                                      |

\* All determinations by x-ray powder photographs.

masses and drusy crystals on specimens from Schneeberg, Saxony and later . . . recognized in massive earthy form on a specimen from Pala, San Diego Co., California." Powder x-ray photographs established the material as a valid species, distinct from bismutite and other secondary bismuth minerals. The mineral was suggested to be a carbonate of bis-

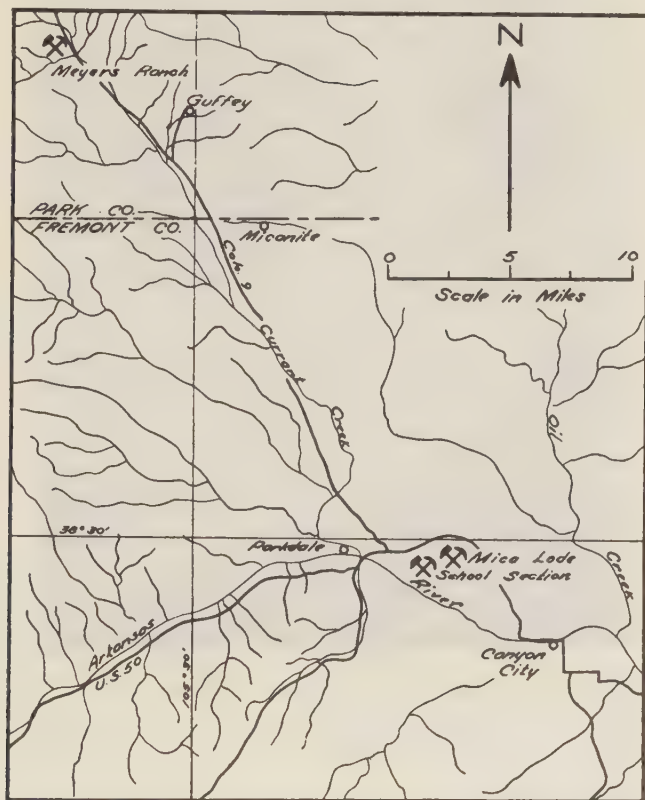


FIG. 1. Index map showing location of beyerite-bearing pegmatites in south-central Colorado.

moth and calcium but a chemical analysis could not be made because of insufficient material. As noted by Frondel (p. 533), an unnamed mineral from Schneeberg described in 1899 by Arzuni and Thaddéeff was probably beyerite, and another described by Bodenbender (1899) from Sierra de Santa Luis, near La Toma in Argentina may also have been that species. The latter material was obtained from a pegmatite dike, 6 to 10 centimeters wide, that contains quartz, feldspar, muscovite, and columbite. The bismuth carbonate occurs as yellow coatings and aggregates.



FIG. 2. Open cut in core-margin replacement unit, Meyers Ranch pegmatite, Park County, Colorado; *m*—fracture-controlled muscovite, *a*—albite, *q*—massive quartz of core. *b*—location of largest bismutite-beyerite mass.

The analysis by Bodenbender is as follows:  $\text{Bi}_2\text{O}_3$  80.7%,  $\text{CO}_2$  8.7%,  $\text{H}_2\text{O}$  1.9% (variable),  $\text{CaO}$  6.7%,  $\text{MnO}$  0.8%,  $\text{FeO}$  0.3%,  $\text{Ce}_2\text{O}_3$  0.54%.

#### COLORADO OCCURRENCES OF BEYERITE

##### *General*

As shown in Table 1, beyerite was found in three deposits: the School Section and Mica Lode pegmatites of the Eight Mile Park area in Fremont County and the Meyers Ranch pegmatite in Park County. The location of these pegmatite bodies is shown in Fig. 1. In all three beyerite is a very rare mineral and occurs intimately associated with bismutite, with which it formed contemporaneously.

*Meyers Ranch pegmatite*

The Meyers Ranch pegmatite is in Park County on the west side of Colorado highway 9, northwest of Guffey (Heinrich and Hanley, 1943, and Hanley, 1946). The body is lens-shaped with inward-dipping foot-wall contacts. A core of white to pink quartz and blocky microcline is enclosed in a wall zone of medium-grained quartz and microcline. Along the contact between the two zones there has been formed a replacement unit that consists of albite, muscovite, beryl, columbite, and black tourmaline. Much of the muscovite in this unit occurs as fracture fillings and tabular fracture-controlled replacement bodies (Fig. 2). Several masses of bismuth carbonates were found in the massive quartz along the contact with the replacement unit. The largest, a wedge-shaped, highly fractured mass about 8 inches long, contained about five pounds of the minerals (Fig. 2).

This material, which consists of very intimately intergrown beyerite and bismutite, is gray, buff yellow, and brown in color and has an earthy to locally waxy texture. The beyerite and bismutite cannot be distinguished megascopically; indeed the presence of the former was not suspected until the characteristic lines were found in *x*-ray powder photographs.

*X*-ray powder photographs of seven different samples indicate that most of the material consists of about 90–95% bismutite and 5–10% beyerite. One of the samples, which photographs showed to be at least 95% beyerite, was selected for analysis (Table 4).

No vestiges of the original bismuth mineral were found. The original material appears to have formed as a late hydrothermal mineral, selectively replacing fractured quartz along the margin of the massive quartz core.

*Eight Mile Park area*

The geology of this area and its pegmatite bodies has been described by the writer (Heinrich, 1947). Bismutite was found in four of the deposits (Table 1) and beyerite in two of the largest pegmatites, the School Section and the Mica Lode (Fig. 3).

At the School Section quarry one- to two-inch nodules of gray bismutite occur with albite, muscovite, and black tourmaline in a replacement unit around a core pod of quartz and blocky microcline. Associated with the bismuth carbonate are secondary chalcocite and its alteration product, malachite. Rare, minute blebs of a white metallic mineral scattered throughout the chalcocite were found to be native silver by means of an *x*-ray powder photograph. *X*-ray powder patterns also indicate



that the bismutite contains intergrown beyerite in minor quantities. A separation of the two minerals was not feasible.

In the Mica Lode pegmatite bismutite and beyerite are somewhat more abundant. They occur together in 2-inch pods, within aggregates of large blades of wedge muscovite. Some of the nodules are pure bismutite, some contain both bismutite and beyerite intimately intergrown, and some are pure beyerite. Those containing only beyerite are generally waxy in



FIG. 3. Open cut in the Mica Lode pegmatite, Eight Mile Park, Fremont County, Colorado.

texture and greenish-gray in color, whereas the bismutite and bismutite-beyerite nodules are gray in color and characteristically earthy in texture. An analysis of beyerite from this pegmatite is given in Table 3.

The carbonates and associated muscovite aggregates occur as part of a pegmatite unit of albite-oligoclase, muscovite, beryl, and triplite which has been formed by replacement of the footwall half of a large microcline-rich core. Locally associated with the bismuth minerals is malachite-stained chalcocite, which also occurs elsewhere in the unit in six-foot masses intergrown with spessartite garnet. Traces of native bismuth occur in chalcocite.

#### MINERALOGY OF BEYERITE

The properties of Colorado beyerite as determined by the writer are in close agreement with those listed by Frondel (1943, pp. 532-533) for the type material from Schneeberg. The following is a composite, generalized description of the mineral:

Bright yellow in crystals, white, gray-green, and gray in massive form; white streak; waxy to vitreous luster;  $G=6.08-6.56$ ; no cleavage observed; effervesces in dilute HCl; uniaxial negative or rarely anomalously

biaxial with a very small  $2V$ ;  $\omega = 2.11-2.15$ ,  $\epsilon = 1.94-1.99$ ; pleochroism absent;  $a_0 = 3.78$ ,  $c_0 = 21.77$ , and  $a_0:c_0 = 1:5.759$ ; tetragonal centrosymmetrical ( $D_{4h}$ ); primitive space lattice type.

Before chemical analyses were begun spectrograms were made by Dr. John C. Rabbitt in order to determine the major constituents:

TABLE 2. SEMI-QUANTITATIVE SPECTROGRAPHIC ANALYSES OF BEYERITE

|                                | Mica Lode         | Meyers Ranch      |
|--------------------------------|-------------------|-------------------|
| BeO                            | .03%              | —                 |
| Bi <sub>2</sub> O <sub>3</sub> | major constituent | major constituent |
| Cr <sub>2</sub> O <sub>3</sub> | —                 | —                 |
| Co <sub>2</sub> O <sub>3</sub> | —                 | —                 |
| CuO                            | 0.6%              | .01%              |
| HgO                            | —                 | —                 |
| MnO <sub>2</sub>               | 0.1%              | .02%              |
| MoO <sub>3</sub>               | —                 | —                 |
| NiO                            | —                 | —                 |
| PbO                            | 2%                | 1.5-2.0%          |
| SnO                            | —                 | —                 |
| CaO                            | >5%               | >5%               |

TABLE 3

|                                | 1     | 2      | 3    | 4    |
|--------------------------------|-------|--------|------|------|
| Bi <sub>2</sub> O <sub>3</sub> | 73.65 | 75.29  | .162 | 1    |
| CaO                            | 8.85  | 9.05   | .161 | 1    |
| PbO                            | 1.73  | 1.77   | .007 | .168 |
| CuO                            | 1.10  |        |      |      |
| MnO                            | 0.12  |        |      |      |
| CO <sub>2</sub>                | 13.59 | 13.89  | .316 | 2    |
| Insol.                         | 0.79  |        |      |      |
|                                | 99.83 | 100.00 |      |      |

1. Analysis of beyerite from Mica Lode pegmatite, Eight Mile Park, Colorado, by F. A. Gonyer.

2. Analysis recalculated to 100% for Bi<sub>2</sub>O<sub>3</sub>, CaO, PbO, and CO<sub>2</sub>.

3. Weight percentages divided by molecular weights.

4. Oxide ratios.

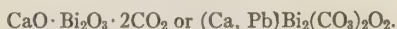
The spectrogram of the Meyers Ranch material also showed strong lines for Si, and weak to very weak lines for Ag, Fe, and Mg.

A sample of beyerite from the Mica Lode pegmatite was prepared for analysis by crushing selected parts of nodules and carefully hand picking fragments beneath the binocular microscope. A powder  $x$ -ray photograph of a portion of the two-gram sample showed that the material was nearly

pure beyerite; bismutite lines were absent. Microscopic examination disclosed the presence of a small amount of quartz, less than 1%. This sample was then analyzed (Table 3).

A two-gram sample from the Meyers Ranch deposit was prepared in a similar manner. Microscopic examination showed that less than 1% of quartz was present, but that bismutite was present in a somewhat larger quantity. The two minerals could not be separated by hand picking or the usual gravimetric methods. An x-ray powder photograph of the sample did not reveal bismutite lines; probably the percentage of bismutite present as an impurity was of the order of 5%. The analysis of this sample is given in Table 4.

The formula of beyerite is therefore:



Lead appears to substitute to a very limited extent for calcium. Lead was also detected spectrographically in the Pala, California, beyerite (Fron-del, 1943, p. 533). With the use of the cell dimensions and gravity measured on the Schneeberg crystals the number of molecules in the unit cell can be calculated:

$$n = \frac{\text{VGN}}{\text{M}}$$

$$n = \frac{(3.78)^2(21.77)(10)^{-24}(6.56)(.606)(10)^{24}}{610.08}$$

$$n = \frac{1234.89}{610.08} = 2.02 \text{ molecules per unit cell.}$$

Differential thermal analyses of bismutite (Petaca, N. M.) and beyerite (Mica Lode, Colo.) have been made by Dr. Carl W. Beck (1946, pp. 112, 114) who reports the following characteristics: for bismutite the curve consists of two merging endothermic curves. Decomposition begins at 400° C., reaches a peak at 530° C. and merges with the second curve which reaches a peak at 625° C., shoulders at 650° C. and returns to zero deflection at 695°. At 730° C. occurs the inversion of the decomposition product,  $\beta\text{-Bi}_2\text{O}_3$ , to an undetermined polymorph.

The curve for beyerite is considerably different: A large endothermic break begins at 485° C., reaches a peak at 570° C., returns to zero deflection at 625° C. (loss of  $\text{CO}_2$ ). The second deflection, which represents the inversion of  $\beta\text{-Bi}_2\text{O}_3$ , begins at 660° C., attains its peak at 675° C. and returns at 700° C.

TABLE 4

|                                | 1     | 2      | 3    | 4    |
|--------------------------------|-------|--------|------|------|
| Bi <sub>2</sub> O <sub>3</sub> | 76.61 | 78.98  | .169 | 1    |
| CaO                            | 7.44  | 7.67   | .137 | 1    |
| PbO                            | 1.25  | 1.29   | .006 | .143 |
| CuO                            | 0.25  |        |      |      |
| Fe <sub>2</sub> O <sub>3</sub> | 0.84  |        |      |      |
| CO <sub>2</sub>                | 11.70 | 12.06  | .274 | 2    |
| H <sub>2</sub> O               | 0.96  |        |      |      |
| Insol.                         | 0.84  |        |      |      |
|                                | 99.89 | 100.00 |      |      |

1. Analysis of beyerite with minor admixed bismutite, from Meyers Ranch pegmatite, Park County, Colorado, by F. A. Gonyer.
2. Analysis recalculated to 100% for Bi<sub>2</sub>O<sub>3</sub>, CaO, PbO, and CO<sub>2</sub>.
3. Weight percentages divided by molecular weights.
4. Oxide ratios.

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## AN IMPROVED APPARATUS FOR DETECTING PIEZOELECTRICITY

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### ABSTRACT

A simple method of detecting piezoelectricity is of value to the mineralogist as an aid in crystal classification.

An instrument is described which is capable of detecting, qualitatively, the piezoelectric effect in crystals ranging in size from approximately 0.1 mm. to 4 cm., having coupling coefficients from approximately 3% up. The apparatus described is simple to operate, and reliable in performance, having given no spurious indications of activity.

The effect of crystal conditions on sensitivity is discussed, and suggestions given for obtaining optimum performance.

Tables are presented showing the size range, and types of materials detected, and the qualitative agreement between the simple "click" indication of this equipment and the more precise measurement on larger oriented specimens.

A complete schematic diagram along with constructional details is given in the appendix.

In the analysis of crystal structure, accessory information concerning the center of symmetry is always of value. Since the presence of a piezoelectric effect is positive proof of the absence of a center of symmetry it was thought an improved apparatus for detecting piezoelectricity would be of interest to mineralogists as an aid in crystal classification. A comprehensive survey of inorganic materials, for example, demonstrated conclusively that an appreciable percentage of the accepted symmetry classifications reported in the literature are incorrect. The device described in this paper is a modification of that developed by Giebe and Scheibe<sup>1</sup> and has proven to be highly reliable in the survey of piezoelectric materials carried out at the Naval Research Laboratory. The apparatus operates on the principle that a piezoelectric crystal placed in alternating electric field will be set into a relatively large vibration whenever the frequency of the field is the same as a natural resonant frequency of the crystal. If the frequency of the field is varied, a momentary vibration of the crystal will be set up as the frequency passes through any of the resonant frequencies of the crystal. This momentary vibration of the crystal reacts with the exciting electric field and can be made to produce a click in headphones or loudspeaker. The results of the measurements with this apparatus were later checked with more accurate measurements of the activity on larger crystals. In all instances checked there was qualitative agreement between the activity as estimated by the vol-

<sup>1</sup> Giebe, E., and Scheibe, A., A simple method for qualitative indication of piezoelectricity of crystals: *Zeist. Phys.*, **33**, 760-766 (1925).

ume of noise produced in this "Giebe-Scheibe" and the more accurate measurements.

This apparatus has never been known to give a spurious indication; that is, if a click is heard it is a definite indication that the crystal is piezoelectric.

In common with other devices of this type, however, it is subject to limitations and under certain conditions may fail to detect piezoelectricity when it does exist. This may be due to one or more of several causes.

(a) The crystal fragments may be so small that all resonant frequencies lie above the frequency range of the oscillator.

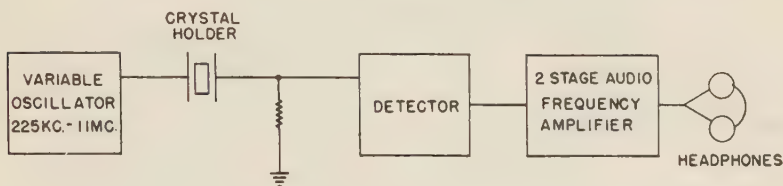


FIG. 1

(b) The electrical and mechanical losses in the crystal may be so large that it is impossible to produce sufficient amplitude of vibration to give an indication.

(c) The crystal fragments may be of such a shape (e.g. needles or plates) that they are not randomly oriented so that the field is not applied in the proper direction to excite the crystal.

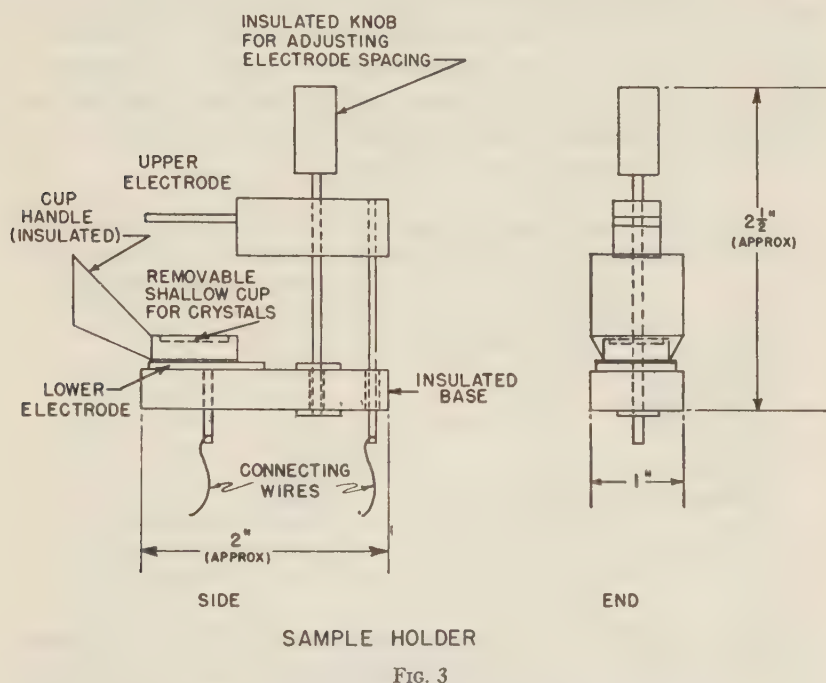
(d) The material may be intimately twinned, thus effectively reducing the apparent size to below that which the apparatus can detect. The effects of these limitations may be minimized by observing certain precautions in making the measurements; and by making full use of the known symmetry data, and any other available information concerning the material tested, which might give a clue to which factors could be masking a piezoelectric effect.

#### DESCRIPTION OF APPARATUS

Figure 1 shows a functional block diagram of the apparatus. The output of the oscillator is placed across the crystal and resistor in series. The voltage across the resistor is rectified and amplified. Any change in voltage across the resistor will have an audio frequency component which will be audible in the headphones. As the slowly changing oscillator frequency approaches and passes a resonant frequency of the crystal, the crystal is set into vibration and undergoes changes in electrical impedance. This causes the voltage across the resistor to vary abruptly which



which is A.C. operated. A complete schematic diagram is shown in Fig. 2. The range was not extended above 11 mc. because the L-C ratio could not be made optimum with the tuning capacitor available, plus the fact that the noise effects increase enormously with frequency above 10 mc. Furthermore, the present range is satisfactory for 100 mesh material in most cases, and tests on smaller particles would be suspect in any event.



#### USE OF THE APPARATUS

In using the apparatus small randomly oriented crystal fragments are placed in the metal holder which is then inserted between the electrodes. No cutting, grinding or electroding of the fragments is necessary as in more refined piezoelectric measurements. If possible tiny and imperfect grains should be avoided. The tuning dial is then turned moderately rapidly until clicks are heard in the headphones. Care should be taken to first use a wide spacing in the crystal holder plates so the field across the crystal will be low. This avoids possible breaking of the crystals. If they are broken by too great an excitation it is not possible to reproduce the click at the same point on the tuning dial because the fracture may result in very small fragments and in extreme cases the response may be lost entirely.



If the precautions in construction discussed in the appendix are observed there should be no "spurious" responses; that is, any click heard is a sign of piezoelectric activity in the crystal and is not due to sudden variation of the oscillator or to other extraneous causes.

If no click is heard over the entire frequency range, factors which might prevent detection of the piezoelectric effect should be considered:

(a) *Size of the fragments.*—The crystal fragments may be too small. The smallest size detectable will depend on the maximum frequency of the oscillator and the frequency constants of the crystal. In general dense, flexible materials may be detected in smaller sizes than light stiff materials. A list of different kinds of crystals which showed piezoelectric activity with their sizes is shown in Table 1.

TABLE 1. TYPICAL SIZES ON WHICH RELIABLE CLICK TESTS HAVE BEEN OBTAINED

| Material                       | Approximate Linear Dimensions             |
|--------------------------------|-------------------------------------------|
| Ammonium dihydrogen phosphate  | 0.1 mm. (100 mesh)                        |
| Quartz                         | 0.2 mm.                                   |
| Twinned quartz                 | 1.5 mm. $\times$ 1.5 mm. $\times$ 0.5 mm. |
| Hemimorphite                   | 1 mm. $\times$ 0.5 mm. $\times$ 0.1 mm.   |
| Iodic acid                     | 0.15 mm.                                  |
| Pentaerythritol                | 0.2 mm.                                   |
| Potassium dihydrogen phosphate | 0.2 mm.                                   |
| Benzil                         | 0.1–0.2 mm. (100 mesh)                    |
| Ammonium oxalate               | 0.1–0.2 mm. (100 mesh)                    |

It should be mentioned that the fragments may be cracked internally so that the effective size is much less than would be estimated.

(b) *Losses in the Crystals.*—Either mechanical losses due to internal friction or electrical losses due to high conductivity might be sufficient to mask a piezoelectric response. Since most crystals have resistivities greater than  $10^7/\text{ohm-cm.}$ , electrical conductivities high enough to be troublesome would not be expected in most crystals unless a conducting layer is formed on the surface by adsorbed moisture.

Presence of a conducting layer due to moisture ordinarily can be detected by a characteristic cracking and popping noise, and in many cases the difficulty can be eliminated by testing in a dry atmosphere.

High conductivities would be expected to be a factor only in semiconducting materials such as some of the oxides and sulfides. The rectification occurring in the semiconducting materials does not in itself produce a click in this apparatus so that there is no more chance of spurious indications than with other crystals.

Mechanical losses sufficient to affect the test are very rare, and would be suspected only in the case of very soft high molecular weight organic materials.

(c) *Improper Orientation*.—The crystal fragments should be randomly oriented. If the original shape is such as to prevent this the fragments should be further broken to permit extensive reorientation.

TABLE 2

| Crystal                                            | Crystal Class   | Estimated Activity<br>"Giebe-Scheibe" | Piezoelectric<br>Coupling in<br>Per Cent |
|----------------------------------------------------|-----------------|---------------------------------------|------------------------------------------|
| CuCl                                               | T <sub>d</sub>  | Active                                | 12*                                      |
| NaClO <sub>3</sub>                                 | T               | Weak                                  | 3                                        |
| NaBrO <sub>3</sub>                                 | T               | Weak                                  | 4                                        |
| KH <sub>2</sub> PO <sub>4</sub>                    | V <sub>d</sub>  | Moderate                              | 11                                       |
| NH <sub>4</sub> H <sub>2</sub> AsO <sub>4</sub>    | V <sub>d</sub>  | Moderate                              | 24                                       |
| NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>     | V <sub>d</sub>  | Strong                                | 30                                       |
| NiSO <sub>4</sub> ·6H <sub>2</sub> O               | D <sub>4</sub>  | Weak                                  | 6                                        |
| NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O | V               | Weak                                  | 5                                        |
| MgSO <sub>4</sub> ·7H <sub>2</sub> O               | V               | Weak                                  | 3                                        |
| ZnSO <sub>4</sub> ·7H <sub>2</sub> O               | V               | Weak                                  | 6                                        |
| HIO <sub>3</sub>                                   | V               | Strong                                | 30                                       |
| KLiSO <sub>4</sub>                                 | C <sub>6</sub>  | Slight                                | 5                                        |
| LiNaSO <sub>4</sub>                                | C <sub>3v</sub> | Slight                                | 8                                        |
| KBrO <sub>3</sub>                                  | C <sub>3v</sub> | Strong                                | 25*                                      |
| MgSO <sub>3</sub> ·6H <sub>2</sub> O               | C <sub>3</sub>  | Weak                                  | 6                                        |
| Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O  | C <sub>2</sub>  | Strong                                | 35                                       |

The piezoelectric coupling factor is a quantitative measure of the piezoelectric activity. The value given in the table is the maximum value for the crystal.

\* Indicates an approximate value from measurements on small cubes.

(d) *Twinning*.—Intimate twinning on a small scale may also mask the piezoelectric effects. Twinned quartz plates, however, which showed no activity on a standard U. S. Army activity meter were easily detected with this apparatus.

Assuming proper attention to technique, the magnitude of the response is reasonably indicative of the piezoelectric sensitivity, because the other properties of the crystal such as mechanical and electrical losses which affect the results are relatively constant in most materials so that the piezoelectric coupling is the factor controlling the amount of response. Table 2 shows a comparison between the response on the small crystal test compared with the results of more refined measurements.

## APPENDIX

*Constructional Details for the Giebe-Scheibe Equipment*

Figure 2 shows the complete schematic diagram of the equipment. A  $10'' \times 14'' \times 3''$  chassis is ample for suitable arrangement of all components. The oscillator and detector components should be placed in a well-shielded compartment. The holder for crystal grains may be placed outside of the shielded compartment. Figure 3 shows a simple crystal holder that is not too difficult to construct. The only front panel controls are the tuning dial, the gain control, the band switch, and the on-off switch.

The oscillator is of the push-pull type (6J6) selected because of its ease of adjustment, and the simple type of tank coil used. The feedback is obtained by means of the 40 *mmf* capacitors connected from the plate of one tube to the grid of the other tube. Switch (*S*) changes bands. (*S*<sub>1,2,3,4,4,6</sub> are ganged.) The purpose of the switch sections are as follows:

- *S*<sub>1</sub> and *S*<sub>2</sub> change grid resistors for class (*C*) bias.
- *S*<sub>3</sub> and *S*<sub>5</sub> select coils, *A*, *B*, *C* or *D*.
- *S*<sub>4</sub> shorts out the unused coils.
- *S*<sub>6</sub> selects tuning capacitor padders.

Band *A* covers the range from 225 KC to 875 KC.

Band *B* covers the range from 875 KC to 2.8 mc.

Band *C* covers the range from 2.75 mc. to 5.8 mc.

Band *D* covers the range from 5.65 mc. to 11 mc.

If mica padding capacitors are used, shunting them with a (1) megohm resistor will reduce dielectric noise. Both sides of the main tuning capacitor are above ground potential; and therefore must be well insulated from chassis and panel. The A.C. voltage across one-half of the tank coil is 150 v. to 200 v. RMS. This is the voltage across the crystal holder. The amount of field across the crystals may be varied by changing the spacing of the crystal holder electrodes. An inverted (6H6) detector is used in order to reduce the effect of the heater-cathode potential on hum output.

Nothing need be said about the audio frequency amplifier and power supply except that they should be carefully arranged and wired so as to eliminate as much noise and hum as possible. It is not recommended that a speaker be mounted in the cabinet because of acoustic feedback effects.

The ultimate sensitivity of the equipment is determined almost exclusively by the noise level. Attention to the following details is necessary in order to minimize noise and to entirely eliminate spurious "clicks" which may be mistaken for crystal activity.

1. The oscillator section and detector elements must be fully shielded

in order to eliminate beat notes with external signals. Beats sound almost the same as clicks, and therefore must be avoided.

2. Oscillator coils must be shielded, and the unused coils shorted out. If this is not done, the natural resonant frequency of the unused coils will absorb energy from the used coil and will also cause "broad" clicks.

3. The tuning condenser rotor should be well grounded to the condenser frame with a short lead.

4. Oscillator components must be adjusted so that no sudden changes in amplitude occur when the frequency is varied. Sudden changes in oscillator amplitude will also cause clicks.

5. The oscillator tube should be shock mounted to avoid microphonic effects.

6. Sometimes simply shorting the coils is not sufficient, for it only succeeds in reducing the " $Q$ ". If shorting is not sufficient a capacitor may be shunted across the coil instead, to place the natural resonance out of the range being used.



## NOTES AND NEWS

### DIFFERENTIAL THERMAL ANALYSIS OF SIDERITE

PAUL F. KERR AND J. L. KULP,

*Columbia University, New York, N. Y.*

Submicroscopic or minutely crystallized siderite is common in a number of important petroleum-bearing sediments occurring in aggregates particularly amenable to the methods of differential thermal analysis. It is a matter of more than ordinary importance, therefore, to clarify the uncertainty which seems to exist concerning the thermal curve of this mineral.

A differential thermal curve of siderite has been published by Cuthbert and Rowland (*Am. Mineral.*, 1947, p. 114). This curve (Fig. 2) shows a broad exothermic peak with a crest at about 560° C. In this laboratory, however, siderite has been observed to yield a strong endothermic peak ranging from 520° C. to 650° C. followed by an oxidation dome. These features are illustrated in the accompanying figure. The curves are representative of those obtained by thermal analysis of 40 siderite samples from the Columbia University collection.

Other laboratories also report endothermic peaks for the thermal curve of siderite as Cuthbert and Rowland have acknowledged in Notes and News (*Am. Mineral.*, 1947, p. 591). However, in explanation these authors state, "Perhaps a fortuitous combination of pure sample, dilution and heating rate has suppressed the endothermic reaction which other workers obtain when these conditions are *different*."

The implication that purity, dilution or heating rate may account for the lack of agreement merits careful consideration. The purity of the Columbia University specimen from the well known Roxbury locality is at least comparable to the anomalous siderite from the same locality described by Cuthbert and Rowland as shown in Table 1. It should be added that all of the samples examined in this laboratory, shown in Fig. 1, have been confirmed by x-ray diffraction.

Dilution with other constituents ordinarily depresses both endothermic and exothermic peaks approximately alike. Grim and Rowland (*Am. Mineral.*, 1942, p. 806) recorded this effect on diluting kaolinite with illite.

Heating rate changes alter the shape or amplitude of a peak (Speil, *U. S. Bureau of Mines, Tech. Paper*, 664, 1945), but do not eliminate an endothermic peak while leaving an exothermic peak unaffected.

Cuthbert and Rowland also explain the curve on chemical grounds as follows: "The exothermic peak is a result of the heat balance between

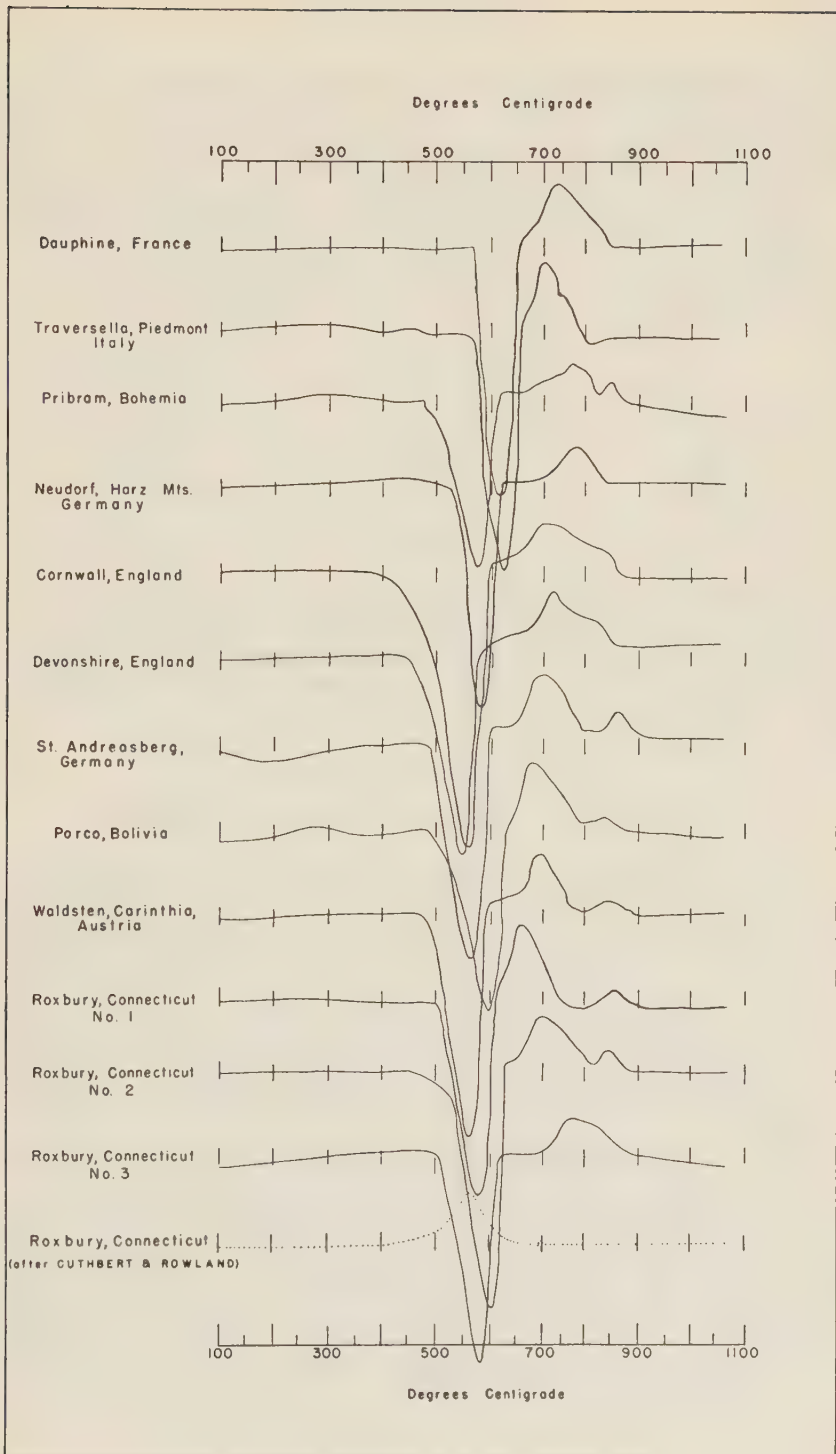


FIG. 1. Differential thermal curves of siderite.

the decomposition of the  $\text{FeCO}_3$  and the immediate oxidation of the resulting  $\text{FeO}$  to  $\text{Fe}_2\text{O}_3$ ." This assumption of "immediate oxidation" is open to question because the decomposition of the tightly packed powder in the thermal well is relatively sudden and the large evolution of  $\text{CO}_2$  in the first few minutes of reaction would prevent the ready access of oxygen to the powder. After the major part of the  $\text{CO}_2$  evolution has ceased, oxidation may proceed as observable in the accompanying curves.

TABLE 1: CHEMICAL ANALYSES OF SIDERITE FROM ROXBURY, CONN.

|               | Cuthbert and Rowland<br><i>Anal. by L. D. McVicker</i> | Kerr and Kulp<br><i>Anal. by Ledoux &amp; Co.</i> |
|---------------|--------------------------------------------------------|---------------------------------------------------|
| CaO           | —                                                      | 0.86                                              |
| MgO           | —                                                      | 4.10                                              |
| FeO           | 53.80                                                  | 56.80                                             |
| $\text{CO}_2$ | 38.21                                                  | 37.25                                             |
| Total         | 92.01                                                  | 99.01                                             |

The cause of the reported exothermic peak is not clear. Neither unusual purity of sample, dilution or change in heating rate appear to furnish an adequate explanation. Until the exothermic peak is confirmed, the primary reaction for siderite should be regarded as endothermic as Cuthbert and Rowland report for other rhombohedral carbonates.

## SYNTHESIS OF TOURMALINE

C. FRONDEL,\* C. S. HURLBUT, JR.\* AND R. C. COLLETTE†

The writers recently have synthesized tourmaline by a hydrothermal method at temperatures in the range from  $400^\circ$  to  $500^\circ$  C. The method employed was based on the recrystallization of powdered tourmaline glass heated in contact with water solutions of magnesium and alkali borates. The largest crystals so far obtained are slender prisms about 0.5 micron in length. Spherulitic aggregates of microcrystals also have been obtained by direct devitrification of the glass under these conditions. Alloy steel bombs basically of the Geophysical Laboratory type were employed.

Tourmaline melts incongruently at temperatures varying roughly from  $1050^\circ$  to  $1200^\circ$  C. for the iron-rich types, the melting temperature decreasing with increasing content of iron or magnesium. Homogeneous glass can be prepared from high-iron tourmaline by quenching from about  $1550^\circ$ . The point of complete melting of lithia-tourmaline, however, is over  $1725^\circ$  C. When the melts approach fluidity they boil slightly

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† Baird Associates, Inc., Cambridge, Mass.

due to loss of water (contained as (OH) in the crystal) and give an odor of fluorine. Some  $B_2O_3$  also may be lost. Tourmaline has been synthesized from such glass when no added fluorine was present in the solution, indicating that most or all of the original fluorine can be replaced by hydroxyl. Differential thermal analysis of a black, high-iron tourmaline revealed an endothermal break (melting) at about  $1050^\circ$  C. immediately followed by a sharp exothermal break presumably representing partial crystallization of a transient complete melt. No thermal breaks were observed below  $1050^\circ$  C.

Synthetic tourmaline made at  $500^\circ$  from a high-iron glass with  $G=2.67$  and  $n=1.582$ , prepared by melting black tourmaline with  $G=3.16$  and  $O=1.647$ , was pleochroic in minute crystals and varied in indices with  $O$  for the most part over 1.65. Material with much lower indices, reflecting variation in the composition of the tourmaline, has been made from such glass by adjusting the composition of the solution which effects the re-crystallization.

The work here described is being carried on in the laboratories of Baird Associates, Inc., Cambridge, under a development contract with the Squier Signal Laboratory, U. S. Army Signal Corps, Fort Monmouth, New Jersey.

#### OCCURRENCE OF BARITE AT PILOT KNOB, MISSOURI

ALBERT J. FRANK AND CORNELIUS S. MOYNIHAN,  
*Saint Louis University, Saint Louis 8, Missouri.*

A specimen of felsite containing hematite was found at the top of a chute leading to a dump on the north side of Pilot Knob. The surface of one side of this specimen is covered with a series of vesicles which appear to be gas holes along a flow surface. Almost all of these vesicles contain orthorhombic crystals of colorless barite ranging in size from those barely visible with a hand lens to the largest with a vertical axis almost one half an inch long; nearly all of these can be described as bladed. They were identified optically as they have the correct indices and optic sign of barite. Besides these crystals show characteristic striations parallel to the length and give the yellow-green flame of barium.

Further study has revealed that these crystals can be found *in situ* near the top of the Knob in cavities in a pyroclastic ferruginous agglomerate. Barite crystals were also found *in situ* in cavities in the main pit; the rock here is a hematitic rhyolite porphyry containing a few xenoliths of red rhyolite. Many of these cavities contain quartz crystals with the barite on the quartz and therefore later than the quartz. If the rock was coarse grained, these cavities could be described as miarolitic.



In fact, they probably formed as gas pockets in which the quartz and barite crystallized. Thus the sequence of the mineral formation can be made out, namely, hematite, quartz, then barite.

The barite occurrence at Pilot Knob has been described by Crane (1), who mentions many small white inclusions of barium sulfate in the ferruginous porphyry which gives it a flecked appearance. He also noted light pink barite "cementing joint and bedding planes in the ore and as small crystals lining cavities in the associated rocks" (2). He states that the light pink barite is secondary.

While the occurrence has been noted, its significance has never been adequately discussed. The barite is of magmatic origin as it occurs high up on the Knob in igneous rock beyond any sedimentary cover. In fact these Precambrian porphyry hills were probably all above water during most of the Cambrian. This barite could not have come from the sedimentary rocks of the area as these formations never covered the Knob. Certainly the occurrence is at a sufficient altitude to preclude any artesian circulation as a possible agent of barite deposition.

The barite had the same source as the hematite. Some might say that both hematite and barite are primary, especially in the rhyolite porphyry but much more likely they are due to magmatic ore bearing solutions.

Any argument that the barite has been leached from the surrounding porphyries only strengthens the fact that the barite is magmatic, a fact which Crane seems to have recognized for his white barite without explicitly saying so.

While this occurrence shows that magmatic barite certainly exists in Missouri one must be careful not to hastily conclude that all barite in Missouri has a similar origin, although it does seem more than chance that the order of quartz followed by barite is the same as found by Tarr (3) for the barite district and also for what seems to be a truly magmatic barite vein in granite also found by him (4).

To show the necessity of the care which must be used in regard to origin, mention should be made of a very recent discovery of barite in the Fern Glen Shale of Mississippian age. Quartz geodes occur in the upper green shale bed at Mountain Ridge, Missouri. Study of one of these selected at random revealed that it contained colorless, striated, orthorhombic barite with the correct indices, interference figure, optical sign, etc. The barite rests on quartz crystals, as also does calcite, and undoubtedly the order of mineral deposition is quartz followed by barite and calcite.

Some might argue that this barite is due to rising magmatic waters which were stopped by the shale or met conditions in the shale necessitating precipitation of quartz and barite. While this barite might well be

due to magmatic waters, acceptance of this idea of magmatic origin means acceptance of the difficulty of the passage of these waters through a rather thick sedimentary section. On the other hand a descending meteoric origin requires rocks above the Fern Glen which contain or did contain barite. Any artesian theory inherently has difficulties similar to both of these theories.

Thus the necessity for a reinvestigation as to whether commercial Missouri barite is sedimentary or magmatic, or both, becomes apparent.

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3. TARR, WILLIAM ARTHUR, The barite deposits of Missouri: *Econ. Geology*, **14**, no. 1, 46-67 (1919).
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#### NAMING OF MICROSCOPIC ORE MINERALS

ERNEST E. FAIRBANKS, *158 West St., Biddeford, Maine.*

The microscopical examination of polished ore specimens by means of reflected light frequently reveals opaque or other ore minerals of microscopical dimensions. In order that other investigators may be able to identify such minerals as having been previously described they should receive a special name. Those of us interested in the special subject, mineragraphy, recognize that the usual type of name conflicts with existing rules governing nomenclature. In order to avoid this controversial subject I offer the suggestion that all minerals of homogeneous character from which a considerable amount of mineragraphic data have been obtained, be given a distinctive name accompanied by the prefix "micro." Thus the "micro" prefix can be dropped when and if the mineralogist eventually recognizes the mineral involved as an authentic new species. On this basis the name "dunhamite" which I recently proposed would become "micro-dunhamite." Mineragraphers with whom I have discussed this matter are in hearty favor of some such special designation.

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Abstracts of papers presented at the Second Annual Spring Meeting held at Postgraduate School, U. S. Naval Academy, March 19-21, 1947, are given below.

## THE DETERMINATION OF THE UNIT CELLS AND SPACE GROUPS OF CHILDRENITE, LINDGRENITE AND PROBERTITE BY THE BUERGER PRECESSION METHOD

WILLIAM H. BARNES, *McGill University*.

The unit cell constants and the space groups of childrenite, lindgrenite and probertite have been determined by the Buerger precession method, using copper and molybdenum radiations. The following results have been obtained:

Childrenite:  $\text{AlPO}_4 \cdot \text{Fe}(\text{OH})_2 \cdot \text{H}_2\text{O}$ , orthorhombic,  
 $a = 10.35 \text{ kX}$ ,  $b = 13.34 \text{ kX}$ ,  $c = 6.90 \text{ kX}$ ,  
 $n = 8$ ,  $Bb\alpha(2)$

Lindgrenite:  $2\text{CuMoO}_4 \cdot \text{Cu}(\text{OH})_2$ , monoclinic,  
 $a = 5.60 \text{ kX}$ ,  $b = 14.03 \text{ kX}$ ,  $c = 5.39 \text{ kX}$ ,  
 $\beta = 98^\circ 23'$ ,  $n = 2$ ,  $P2_1/n$ .

Probertite:  $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ , monoclinic,  
 $a = 13.85 \text{ kX}$ ,  $b = 12.54 \text{ kX}$ ,  $c = 6.60 \text{ kX}$ ,  
 $\beta = 107^\circ 40'$ ,  $n = 2$ ,  $P2_1/n$ .

This work was carried out in Professor M. J. Buerger's Laboratory of X-Ray Crystallography at the Massachusetts Institute of Technology during the tenure of a Fellowship from the John Simon Guggenheim Memorial Foundation.

## THE STRUCTURE OF DIGLYCINE HYDROBROMIDE

ELSA BARNEY, *Massachusetts Institute of Technology.*

The Weissenberg method was used to determine the space group,<sup>1</sup>  $D_2^4$ , and the unit cell of  $a = 8.21 \text{ \AA}$ ,  $b = 18.42 \text{ \AA}$ , and  $c = 5.40 \text{ \AA}$ . The cell contains 4 ( $\text{C}_4\text{H}_{11}\text{BrN}_2\text{O}_4$ ).

For the determination of the parameters, the intensities of  $hk0$ ,  $0kl$ , and  $h0l$  reflections were determined by Dawton's method. The Weissenberg method using  $\text{CuK}\alpha$  radiation was used to obtain the  $hk0$  and  $h0l$  reflections. The precession method, using  $\text{MoK}\alpha$  radiation, was used to obtain the  $0k$  reflections. From Patterson summations the bromine atom was located and by assuming that the bromine atom determined the phases, electron density maps  $\rho(xy0)$ ,  $\rho(0yz)$  and  $\rho(x0z)$  were made. These gave the locations of other atoms. However, which of these locations were for oxygen, which for nitrogen, and which for carbon, could not be ascertained from the relative heights of the electron density peaks, as the difference of scattering power of oxygen, nitrogen, and carbon is small. The peaks that represented the O, N, and C were decided upon by assuming the diglycine structure to be built up of glycine molecules of known structure.<sup>2</sup>

Further refinement is necessary on the atomic positions listed.

|    | $x$  | $y$  | $z$  |
|----|------|------|------|
| C  | .089 | .380 | .833 |
| C  | .106 | .430 | .120 |
| O  | .470 | .112 | .317 |
| O  | .196 | .333 | .842 |
| N  | .268 | .430 | .158 |
| Br | .178 | .035 | .833 |
| C  | .423 | .283 | .517 |
| C  | .065 | .172 | .373 |
| O  | .475 | .213 | .650 |
| O  | .423 | .283 | .350 |
| N  | .145 | .193 | .158 |

<sup>1</sup> Space group determined by M. J. Buerger.

<sup>2</sup> Albrecht, G., and Corey, R., *J.A.C.S.*, **61**, 5 (1939).



**AN ELECTRONIC METHOD OF FOURIER SYNTHESIS**

L. S. BIRKS, *Naval Research Laboratory.*

Fourier synthesis by the Bragg method is accomplished using a television receiver for projection of the individual terms in the series. Continuous, rather than stepwise variation in the amplitude, phase, and wavelength of the cosine terms is possible with equipment consisting of a television receiver and a stable oscillator of continuously variable frequency. A rotatable camera mount makes possible the addition of the individual terms in the proper direction with respect to the unit cell axes. About one-half hour is required to sum up a hundred terms.

**AN ALINEMENT CHART FOR THE POLARIZATION CORRECTION IN THE EQUI-INCLINATION WEISSENBERG METHOD**

W. L. BOND, *Bell Telephone Laboratories.*

An alinement chart is presented for use with the equi-inclination Weissenberg method. The chart gives the polarization correction directly from the layer line screen setting and the distance of the reflection from the zero line.

**MAKING ORIENTED CRYSTAL PLATES FOR PIEZOELECTRIC INVESTIGATIONS**

W. L. BOND, *Bell Telephone Laboratories.*

Crystals the size of sand grains, and known to be of low symmetry, are tested by the Geibe and Scheibe method. If active they are grown to pea size and three mutually perpendicular plates cut (arc holder in conoscope). These are tested for electro mechanical coupling by a bridge method. If this is high, the crystal is grown to hazelnut size, and sets of plates are cut oriented with respect to the crystallographic axes using x-rays. These are used to determine the elastic constants, piezoelectric constants, and expansion coefficients.

**THE GENESIS OF CRYSTAL FORMS AND A RATIONAL EXPLANATION OF THE "LAW" OF BRAVAIS**

M. J. BUERGER, *Massachusetts Institute of Technology.*

A number of rules have been proposed to correlate the relative importance of the several faces of a crystal with the geometrical features of the crystal lattice. Chief of these are the rule of simplest indices, Bravais' rule, and Donnay-Harker's rule. The latter has had considerable success in formulating the relative importance of the faces of a crystal, but it is completely empirical, as are the other rules. This paper suggests a rational explanation as to why the rule should work. It is shown that if the crystal grows by accretion of molecular chunks which are equivalent by an operation with a translation component, then Bravais' rule can be derived from crude surface energy considerations. These considerations also explain the stability of crystal faces and predict that crystals may sometimes form without faces when they grow from media of equal surface tension. The same theory accounts for the known deviations from Bravais' rule by ionic crystals.

**THE LATTICE CONSTANTS OF A SINGLE CRYSTAL OF BARIUM TITANATE**

A. P. DEBRETTEVILLE AND S. BENEDICT LEVIN, *U. S. Signal Corps.*

Weissenberg moving film layer photographs were taken of a barium titanite crystal of about 1 mm. size. The crystal was synthesized by crystallization from a melt. The

zero-level photographs show barium titanite has a simple tetragonal lattice with one formula weight per unit cell, and with lattice constants  $a=3.99 \text{ kX}$ ,  $c=4.03 \text{ kX}$ , giving  $c/a=1.01$ . This provides direct confirmation of constants indirectly determined by Megaw on polycrystalline material, on the basis of an assumed  $c/a=1.01$  with  $a=3.9860 \text{ kX}$  and  $c=4.0259 \text{ kX}$ . The density calculated from  $x$ -ray data is 6.00. Direct measurement on the single crystal material yields 5.78. Our powder measurements give  $a=3.982 \text{ kX}$  on the basis of  $c/a=1.01$ .

Superposition of the  $a$  and  $c$  reflections on the same central layer lattice lines indicate that the apparent single crystal is actually composed of many small units whose  $c$  axes lie in all three directions formerly occupied by the  $a$  axes of the antecedent cubic barium titanite above  $120^\circ\text{C}$ . (the Curie point).

## PHYSICAL CHEMICAL PHENOMENA IN CRYSTAL GROWTH

PAUL H. EGLI AND PAUL L. SMITH, *Naval Research Laboratory*.

A useful picture of crystal growth which fits many of the experimental facts has been developed from the concepts of Kossel, Stranski and Landau.

Features of the crystallization process accounted for include supersolubility, superheatibility of nuclei effects of foreign ions, and the effect of temperature, etc.

Application of this picture to growth both from melts and from solution has suggested useful techniques in the preparation of large single crystals.

Although the picture is by no means complete, the success of these techniques developed from it contributes additional evidence concerning parts of the theory of crystal growth which are not yet settled.

## X-RAY CRYSTALLOGRAPHY OF SOME HETEROPOLYMOLYBDATES

HOWARD T. EVANS, JR., *Massachusetts Institute of Technology*.

The heteropolymolybdates are ionic oxy salts of which the anion is generally very large and complex. The anion contains a number of highly condensed  $\text{MoO}_6^{6-}$  octahedra with a coordinated metalloid ion forming a nucleus. Three distinct structural types are well known: the 12-molybdates (i.e.,  $\text{SiMo}_{12}\text{O}_{40}^{3-}$ ), the 9-molybdates (i.e.,  $\text{PMo}_9\text{O}_{31}^{3-}$ ), and the 6-molybdates (i.e.,  $\text{IMo}_6\text{O}_{24}^{5-}$ ). Of all the iso- and heteropoly salts, the only type whose structure has been studied and worked out is the first of these. The subject of the present study is the structure of the hetero-6-molybdates.

The present report gives a preliminary account of a lattice study of several compounds of this type. The data found are as follows:

- (1)  $(\text{NH}_4)_6\text{TeMo}_6\text{O}_{24} \cdot \text{H}_6\text{TeO}_6 \cdot 7\text{H}_2\text{O}$ : monoclinic, space group  $A2/a=C_{2h}^6$ ;  $a_0=21.38 \text{ \AA}$ ,  $b_0=10.01 \text{ \AA}$ ,  $c_0=18.75 \text{ \AA}$ ;  $\beta=115^\circ 30'$ ;  $Z=4$ .
- (2)  $(\text{NH}_4)_6\text{TeMo}_6\text{O}_{24} \cdot 7\text{H}_2\text{O}$ : orthorhombic, space group  $Pnaa=D_{2h}^{10}$ ;  $a_0=14.64 \text{ \AA}$ ,  $b_0=14.92 \text{ \AA}$ ,  $c_0=13.96 \text{ \AA}$ ;  $Z=4$ .
- (3)  $\text{K}_6\text{TeMo}_6\text{O}_{24} \cdot 7\text{H}_2\text{O}$ : isomorphous with (2);  $a_0=14.26 \text{ \AA}$ ,  $b_0=15.04 \text{ \AA}$ ,  $c_0=14.53 \text{ \AA}$ . Space group  $Pnna=D_{2h}^{10}$ .

The pseudocubic habit of all these compounds is quite striking. The morphology of (2) and (3) has been studied previously by Donnay and Melon,<sup>1</sup> and the data above show some departure in detail from their results.

Four other isomorphous compounds have been incompletely studied in this series.  $(\text{NH}_4)_3\text{H}_3\text{XMo}_6\text{O}_{24} \cdot 12\text{H}_2\text{O}$ , where  $\text{X}=\text{Al}$ ,  $\text{Fe}$ ,  $\text{Cr}$ , and  $\text{Co}$ . These crystals are parallelogram plates showing symmetrical extinction.  $X$ -ray patterns show a twinned lattice which is

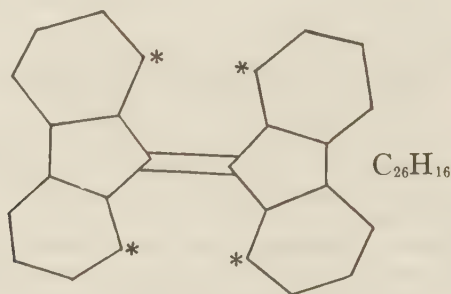
<sup>1</sup> *Proc. Nat. Acad. Sci.*, **20**, 327 (1934).

apparently triclinic. The patterns also show some randomness of structure and seem to be entirely unsuited for accurate intensity measurements.

### PRELIMINARY REPORT ON THE STRUCTURE OF BIS-BIPHENYLENE ETHYLENE

C. P. FENIMORE, *Aberdeen Proving Ground.*

Bis-biphenylene ethylene possesses conjugated double bonds and should therefore be planar.



With the customary bond lengths and angles, however, the starred carbon and hydrogen atoms overlap. A large departure from the usual bond values would be required for planarity. This might be possible (in part at least) if the molecule were a diradical, for which there is some indirect chemical evidence. Other planar structures, not diradical, might be suggested, or the molecule may not be planar at all.

Bis-biphenylene ethylene crystals are acicular, unterminated, orthorhombic, *Pcan*;  $a=17.2$ ,  $b=36.9$ ,  $c=8.23$ ;  $Z=12$ .

The decreasing order of interplanar distances  $d_{(hkl)}$  is 020, 110, 130, 200. According to the generalized law of Bravais this should be the order of the relative importance of the corresponding forms. The crystals are morphological anomalies, however, in that the single large form is (130) and the only other  $(hkl)$  face is a line face (200).

This anomalous predominance could be explained by placing molecules in

Position 4: (a), symmetry  $\bar{1}$ ; or 4: (c), symmetry 2, with  $x=0$

$$\text{giving } 00z_1, 00z_1+\frac{1}{2}, \frac{1}{2}z_1, \frac{1}{2}z_1+\frac{1}{2}$$

$$[z_1=0 \text{ or } \frac{1}{4} \text{ as position (a) or (c) is used}]$$

and in

Position 8: (d), symmetry 1, with  $x=0$ ,  $y=\frac{1}{2}$ ,

$$\text{giving } 0\frac{1}{3}z, \frac{1}{2}\frac{1}{6}z+z, \frac{1}{2}\frac{5}{6}z, 0\frac{1}{3}z-z, 0\frac{1}{3}z, \frac{1}{2}\frac{5}{6}z-z, \frac{1}{2}\frac{1}{6}z, 0\frac{1}{3}z+z$$

thus forming in projection three centered pseudo cells. Then the order of  $(hkl)$  planes in decreasing importance could be (130), (200) as observed.

In the structure determination, using approximately these positions, the ethylenic bond in (a) or (c) is found to be parallel to the  $a$  axis, in (d) parallel to the  $b$  axis. The molecule appears to be more planar than the usual values for bond lengths and angles would permit.

## HIGH TEMPERATURE-PRESSURE CRYSTAL GROWTH

I. I. FRIEDMAN, *Naval Research Laboratory.*

Crystal synthesis under high temperature and pressure is complicated not only by the inherent difficulty of experimentation under these conditions, but also by the lack of data in the literature. Therefore, the first step in the synthesis of large single crystals under these conditions is to accumulate data concerning systems from which the crystal will crystallize.

The problem can be illustrated by the examples of quartz, aluminum phosphate, and barium oxide. In order to synthesize quartz the ternary system  $\text{Na}_2\text{O-SiO}_2\text{-H}_2\text{O}$  was chosen. The system was investigated from 200°C. to 400°C. In addition to equilibrium data, the rates of solution and growth of quartz under different conditions of temperature and composition was determined. The system exhibits liquid immiscibility which disappears below 200°C. Several methods of growth present themselves. Quartz can be grown by saturating a solution of NaOH with  $\text{SiO}_2$  at 350°C. and lowering the temperature to 250°C., or it can be grown in the quaternary system  $\text{Na}_2\text{O-SiO}_2\text{-H}_2\text{O-CO}_2$ . A discussion of both the ternary and the quaternary system will illustrate the methods.

The aluminum phosphate problem is quite similar and it can be grown in the ternary system  $\text{AlPO}_4\text{-H}_2\text{O-P}_2\text{O}_5$  by several methods.

Several systems from which beryllium oxide may be grown are discussed.

## REPLACEMENT OF CALCITE IN COPPER CHLORIDE

ROBERT M. GARRELLS, *Northwestern University.*

Calcite is covered quickly by a green film when exposed to hot solutions of cupric chloride. The rate of thickening of the film is a logarithmic function of time and of the concentration of the reacting solution. Studies of film formation as a function of temperature yielded data which indicate a possible change of composition of the film. The green film formed under most conditions is atacamite; thus the replacement represents an interesting case in which the replacing substance has no common ions with the original material but in which the rate of replacement is chemically controlled by the original material. Studies also were made of colloidal loss, and curves have been determined for the change in replacement rate for cases intermediate between a completely stable film and a film which is lost as rapidly as it is formed.

## KINETICS OF D.D.T. CRYSTALLIZATION FROM THE MELT

VICTOR GILPIN, *Armour Research Foundation.*

As an outgrowth of the work described in the paper by W. C. McCrone, quantitative measurements were made of the linear crystallization velocity of D.D.T. as a function of temperature, and amount of added impurity. From these data equations were derived which predict growth rates with considerable accuracy at the lower temperatures. Some impurities lower the activation energy of crystallization, others do not. A survey of earlier work shows the dependence of the linear crystallization velocity on the fluidity of the supercooled melt, in the low temperature ranges where the fluidity activation energy is abnormally high. At higher temperatures, where the fluidity activation energy falls to more normal values, fluidity is no longer the rate determining step in crystallization.



### AN X-RAY METHOD OF IDENTIFYING GEMSTONES

SAMUEL G. GORDON, *The Academy of Natural Sciences in Philadelphia.*

The random manner in which gemstones are usually cut, as well as their mounting, has precluded use of conventional X-ray techniques for identification purposes. By simply rotating and oscillating a gemstone in a beam of X-rays with automatic shifting through all possible  $2\theta$  values, reflections should be obtained from a sufficient number of planes to identify it by comparison with a series of standards prepared from the few dozen minerals found in jewelry.

### CHALLENGING PROBLEMS IN CRYSTALLOGRAPHY

DAVID HARKER, *General Electric Research Laboratories.*

Almost all the realms of crystallography present challenging problems. A partial list of problems includes the following:

The development of new methods for crystal structure determination, experimental and theoretical.

A correlation of the properties of crystals with their structures and the application of such correlations to related materials.

A study of crystal imperfections; their origins and their theoretical and practical implications.

The problems of crystal plasticity.

The problems of crystal growth and degrowth.

The problems connected with the nature of solid-solid reactions.

The problems of electrical and thermal conductivity.

The problems connected with piezoelectricity.

The question as to the nature of ferro-magnetic and ferro-electric materials.

The surface properties of crystals: catalysis and electron emission.

All these fields contain unsolved problems inviting the interest and effort of crystallographers. In addition to these problems, there must be many others that have not as yet been even studied.

There is obviously a glorious future in crystallographic research.

### SURVEY OF INORGANIC PIEZOELECTRIC CRYSTALS

LEWIS R. JOHNSON, *Naval Research Laboratory.*

Inorganic crystals reported anywhere in the literature to be in symmetry classes permitting piezoelectricity have been reviewed unless they were obviously valueless because of poor stability or undesirable electrical properties. Most emphasis has been devoted to those compounds which have the most promising composition and electronic configuration. A variety of water-soluble materials have been grown to a stage where semiquantitative measurements of their merit factors could be made using techniques specially devised for measurement of tiny specimens. Oxygen bearing compounds with highly electropositive cations and highly electronegative anions exhibit the most activity, but rigorous correlation of property and structure await extension of our present concepts.

A NEW CRYSTALLOGRAPHIC FORM OF RED PHOSPHORUS<sup>1</sup>GILBERT E. KLEIN, *Massachusetts Institute of Technology.*

When ordinary red phosphorus is heated at various temperatures for varying lengths of time, several distinct crystalline modifications are formed. At a temperature in the neighborhood of 600° C. a new crystallographic form appears. The material is in the nature of hard lumps which are almost opaque under the microscope. No single crystals of size sufficient for measurement could be found.

An x-ray powder photograph of this new crystalline form contains some 26 lines and shows the material to have a simple cubic lattice. The indices of the planes producing the powder lines run out to values as high as (931). Since the indices assigned to the lines show no systematic missing reflections, the possible space groups for this form are:  $P23$ ,  $P43$ ,  $Pm3$ ,  $P\bar{4}3m$ , or  $Pm3m$ , of which only the space group  $P23$  may be ruled out by other considerations.

The size of the unit cell edge is calculated to be equal to  $11.29 \text{ } kX$ , and using the measured value for the density of the material as being 2.38, the number of atoms per unit cell is calculated to be 66.

<sup>1</sup> Published with permission of the War Department. This work was conducted under research contract with the Chemical Corps, United States Army.

## THE EPSILON FORM OF SOME SODIUM 1-ALKANESULFONATES

F. C. LINGAFELTER AND L. H. JENSEN, *University of Washington.*

Six distinct crystalline hydrates of the sodium 1-alkanesulfonates have now been recognized. The  $\epsilon$  form has been found for sodium 1-tetradecane-, 1-hexadecane-, and 1-octadecanesulfonate, by crystallization from solutions in carbon tetrachloride-ethanol-water or 1, 4-dioxane-ethanol-water at *ca* 30°. The triclinic crystals are extremely small, very thin tabular parallel to {001} and outlined by {101} and {011}. The unit cell contains 8 molecules of  $RSO_3Na$  and probably some water of crystallization. The general features of the structure are discussed and compared with the forms previously investigated.

## THE APPLICATION OF CRYSTAL CHEMICAL PRINCIPLES TO THE PROBLEM OF GLASS STRUCTURE

JOSEPH S. LUKESH, *Massachusetts Institute of Technology.*

The structural characteristics of silicate glasses cannot be determined by the usual methods available to crystallographers. The information that can be obtained from x-ray analysis is limited. However, when one applies knowledge of silicate crystals, much useful information may be deduced. Huggins<sup>1</sup> has shown, for instance, that the densities of a series of glasses such as sodium silicate can be represented by straight lines with changes in slope at compositions which have crystal chemical significance. If the densities are plotted as functions of the ratio of silicon atoms to oxygen atoms, the changes in slope appear at the ratios which characterize the different silicate crystalline structural types. A further change in slope occurs for which there is no known type. By considering the densities of the various atomic species, it is seen that this break has a different character. It is deduced that the break represents the point at which the essentially cristobalite-like network of silicon and oxygen becomes saturated with sodium atoms.

If one plots the densities of sodium calcium silicate glasses on a three-dimensional

<sup>1</sup> Huggins, M. L., *Jour. Opt. Soc. Am.*, **30**, 420 (1940).

graph as functions of the ratios Na/O and Ca/O, the surface is found to be made up of a group of planes. A tentative structure-phase diagram can be constructed from published data. The boundaries of the planes appear to follow the crystalline silicate type compositions.

### AN EASILY MADE TWO-CIRCLE GONIOMETER

A. S. MAKAS AND C. D. WEST, *Research Laboratory, Polaroid Corporation.*

Modern crystal measurement consists primarily in first determining the  $x$ -ray elements, diffraction symbol, and possible space groups for a given single crystal, and then showing that the measured angular coordinates of all of the observed growth faces are consistent with these elements and space groups. The crystals used are small and often have faces of poor quality. A goniometer is a practical necessity, first for shortening the time needed to set up the crystal for the  $x$ -ray measurements, second for determining the two angular coordinates of each growth face, and third because the facial symmetry may contribute to the correct choice of space group. American crystallographers are at a disadvantage because a rational instrument has not been previously designed for these purposes and made in this country.

Students' spectrometers allowing readings to  $1'$  on a horizontal circle are however readily available in this country at moderate prices. Representative optics of such instruments include objective lenses of 150 mm. focal length and an autocollimating Ramsden eyepiece of 25 mm. focal length, the combination being a  $6\times$  telescope. Such instruments could be simply converted to one-circle goniometers by replacing the collimator slit with an interchangeable signal system, by adding a short-focus flip-out lens in front of the telescope objective that will change it at will to a microscope magnifying about  $30\times$ , and by providing a holder for the goniometer head used in Weissenberg cameras. It is also desirable to make an alternative eyepiece of lower power, say 100 mm. focal length to give a lower magnification with crystal faces of poor quality.

Since it is generally agreed that one-circle goniometers are inadequate for modern crystal measurement, we have converted the spectrometer just specified directly into a two-circle instrument. This requires only the extra steps of placing the microscope-telescope system on a fixed post so that its axis intersects that of the collimator at an angle of about  $60^\circ$ , and putting in its place on the moving arm a properly counter-weighted vertical circle assembly, preferably reading also to  $1'$  and carrying the goniometer head. This system can be put and kept in adjustment without difficulty, and appears to be adequate for the purposes stated in the first paragraph. Further elaborations such as the telescope systems of V. Goldschmidt could be incorporated without difficulty if desired, but they do not seem necessary at present.

### SOME OBSERVATIONS ON CRYSTAL GROWTH FROM THE MELT

W. C. McCrone, *Armour Research Foundation.*

This paper will summarize the data on the use of the crystallization rate of DDT for the quantitative analysis of technical mixtures. The assumption was made in the course of this early work that synthetic mixtures of the two principal isomers of DDT would be equivalent to mixtures of technical DDT containing the same amount of  $p,p'$ -isomer. In other words, that  $o,p'$ -DDT would have the same effect on the rate of crystallization of  $p,p'$ -DDT as an equivalent amount of the various isomers and by-products known to be present in the technical products. Although this turned out to be correct, on the basis of comparative analyses, the question naturally arises as to whether the decrease in growth rate on addition of impurity is, in general, independent of the nature of the impurity.

The present study was undertaken, therefore, in an effort to determine the effect of the nature of the impurity on the rate of crystallization of *p,p'*-DDT. These studies have shown that the nature of the impurity has a very large effect on the rate of crystallization. For example, at 34° C. a mixture of 80% *p,p'*-DDT—20% *p'*-DDT grows at a rate of 80 microns in 5 minutes; a mixture of 80% *p,p'*-DDT—20% thymol at a rate of 2440 microns in 5 minutes; and a mixture of 80% *p,p'*-DDT—20% triphenylbenzene at a rate of 35 microns in 5 minutes.

Further work has been done to determine what physical properties (of the impurity) are significant in their effect on growth rates. A number of properties such as heat of crystallization, heat conductivity, molecular shape and size, and viscosity were investigated with the result that viscosity has been shown to be the principal factor in this particular case, that is, the crystallization of *p,p'*-DDT from the melt.

### THE OSCILLOGRAPHIC FOURIER SYNTHESIZER<sup>1</sup>

R. PEPINSKY, *Alabama Polytechnic Institute.*

The design and operation of an electronic synthesizer for two-dimensional Fourier series is discussed and illustrated. Operation of the synthesizer is based upon Bragg's early method for photographic summation of simulated interference fringes. The required sinusoidal light intensity variations are produced on the screen of a cathode ray tube by means of a television scan and intensity modulation of the CR tube grid, and the light pattern is locked in position by complete synchronization of modulation and sweep signals.

Amplitudes of Fourier coefficients are supplied to the machine as settings of individual volume controls, and phases (0° and 180°) are entered by means of double-throw switches for each term. A complete centro-symmetric planer projection of electron densities, corresponding to a specific set of amplitude and phase values, appears on the screen once each scanning frame. The projection remains on the screen as long as is desired. Effects of changes in phase of one or any number of terms, by changing the switch position for each term involved, are immediately observable on the screen—as are effects of individual amplitude changes.

Projections of any desired axial ratio or angle are readily attainable.

The synthesizer is designed to facilitate the deduction of general features of a structure, through alleviation of the tediousness of trial-and-error stages of an analysis. Because of the rapidity with which the effects of phase changes are observable, systematic variations of Fourier coefficient signs becomes possible in the search for a self-consistent structure.

<sup>1</sup> This is a development of the technique first reported by the writer at the Lake George, N. Y., meeting of the *A.S.X.-R.E.D.*, June 11, 1946.

### MICROSCOPIC IDENTIFICATION OF TWO "LIQUID CRYSTALLINE" SOAP PHASES: NEAT SOAP AND MIDDLE SOAP

F. B. ROSEVEAR, *The Procter & Gamble Company.*

Neat soap and middle soap are two "liquid crystalline" (anisotropic liquid, mesomorphic, paracrystalline) aqueous solution phases which are important in the manufacture of soap and synthetic detergents.

Over the twenty years since McBain and Langdon announced middle soap as a phase distinct from the neat soap of soap boiling operations, ultimate distinction between the two has depended almost solely upon the comparative fluidity of neat soap and the strikingly



stiff plasticity of middle. There are, however, cases where the fluidity test is not adequate, as, for example, where the two phases are mixed with each other or with other phases. Apparently because both are considered to be typical "conic anisotropic liquid" or "smectic" phases, no generally applicable method for distinguishing them optically has been proposed.

In the work here reported, examination with the polarizing microscope has shown that while middle soap is characterized by the relatively coarse and well developed focal conic structure recognized since McBain's earliest papers on this phase, neat soap characteristically exhibits the texture described in the liquid crystal literature as "oily streaks," or a related texture consisting of individual or densely packed liquid spherulites. Almost always, considerable portions of the neat phase are isotropic because of orientation of the soap molecules perpendicular to slide and cover glass. The neat-middle distinctions are illustrated by photomicrographs, including some of the compositions generally accepted as being representative of each phase.

There is a phase termed neat soap occurring in many anhydrous soaps near 200–300° C. The work of McBain, the Volds, and their colleagues indicates that this phase is not continuous with "soap boiler's neat," as had been assumed in earlier work. Since there is sufficient evidence already published to show that the anhydrous neat soap is characterized by well developed focal conic structure, the properties here presented for "soap boiler's neat" serve as additional evidence for discontinuity between these two phases.

### SENSITIZED LUMINESCENCE

JAMES H. SCHULMAN, *Naval Research Laboratory.*

The ultraviolet excited luminescence of most inorganic crystalline phosphors is due to small amounts of impurity (activator) in solid solution in the host crystal. In the simplest case the activator may be considered to act like a dilute gas of atoms or ions, which absorb ultra-violet radiation incident upon them from an external source and re-emit the absorbed energy as luminescence. In other cases the absorption of the exciting energy takes place in the atoms of the host crystal and this energy is subsequently transferred to the activator, which then emits luminescent radiation.

A situation of particular interest arises if two impurities are built into the crystal, one of which functions as the absorber ("sensitizer") of the exciting radiation, and the other as the emitter. In this way phosphors can be built which are excited by selected regions of the ultraviolet. Examples of phosphors showing "sensitized" luminescence are the manganese-activated alkali halides and calcite, and certain rare earth activated sulfides.

### HARDNESS VARIATION AND THE MICROSTRUCTURE OF THE DIAMOND

C. B. SLAWSON, *University of Michigan.*

Microscopic twinning lamellae and polysynthetic twinning are characteristic of the diamond. Because of the differential hardness, twinning lamellae stand out in relief on a polished surface when examined with the reflecting microscope, if the direction of polishing is properly oriented. A diamond megascopically twinned on (111) may have other twinned structures on (111), ( $\bar{1}\bar{1}1$ ), and (1 $\bar{1}$ 1). The apparent greater hardness of some diamonds as observed by diamond cutters may be explained by twinning lamellae. Contrary to the general practice in industry these so-called hard diamonds will be undesirable for tools. The twinning lamellae will become zones of inferior hardness on the working surface of the tool.

## TWINS AND INTERGROWTHS

DOROTHY WRINCH, *Smith College.*

The possibility that twins and intergrowths of crystals, supplementing crystalline form and atomic composition, may yield indications regarding their internal structure, is suggested. This approach is being developed for use in extremely complicated crystals where x-ray intensity data are not available. To demonstrate it, staurolite is chosen as an example, since its atomic structure is well-known.<sup>1</sup>

From measurements of angles between faces, Dana derives an orthorhombic unit cell, with axial ratio  $a:b:c=0.4734:1:0.6828$  and 032,232,230 and 130 as twinning planes.<sup>2</sup> Since the ratios differ from 2:3, 2:2 by less than 2.5 per cent, we introduce a submultiple cube of edge  $k$  (following many precedents) and write as an approximation

$$a=2k, b=3k\sqrt{2}, c=2k\sqrt{2},$$

thus taking cubic axes XYZ defined by

$$X=2x, Y=3y-2z, Z=3y+2z,$$

with the unit cell of volume  $24k^3$ . The unit cell faces are then translated into  $(100)_c$ ,  $(011)_c$  and  $(0\bar{1}1)_c$  of the cubic system and the twinning planes correspondingly into  $(001)_c$ ,  $(101)_c$ ,  $(211)_c$  and  $(111)_c$ . Let us call a cube face an X-plane, a face of the icositetrahedron, the rhombic dodecahedron and the octahedron of the cube, a U-, a V- and a W-plane. The staurolite twins are then seen to be expressible in terms of the cube as X, U, V and W twins. Their existence confirms what is already suggested by the cell ratios; namely, that—to some high degree of approximation—the crystal contains some *major cubic theme*, that this theme is of the scale and in the orientation of the submultiple cube and that there is also present some *minor non-cubic theme*, which so far as the cube is concerned is referred to a super or multiple lattice. According as the major theme lies on a cubic network or on a body-centered or face-centered cubic network, the cube contains 1, 2 or 4 repetitions and the orthorhombic cell 24 times as many. The major theme provides sites for the members of the minor theme in cubes, in octahedra and in octahedra and tetrahedra respectively: not all these sites are tenanted, when they are the surrounding polyhedra are slightly distorted.

If information regarding composition is now added; namely, Dana's suggestion of  $\text{HFeAl}_3\text{Si}_2\text{O}_{13}$ , in which we see that  $\text{O}_{13}$  must be corrected to  $\text{O}_{12}$ , we identify the cubic theme as an oxygen network. We select the face-centered network in order to provide tetrahedral sites for silicon and deduce 8 such units for Dana's unit cell. The X- and V-twins have an undisturbed network: the U- and W-twins adjoin the face-centered cubic networks in hexagonal closest packing. In all, the minor non-cubic theme is disturbed and the existence of twins is explained. The data have thus suggested what is known from x-ray studies to be the correct structure so far as it goes, leaving undetermined only the selection of positions from among the octahedral and tetrahedral sites for the minor theme. (This step follows from the space-group which also further corrects the composition into  $\text{H}_2\text{FeAl}_4\text{Si}_2\text{O}_{12}$ . It may be mentioned that the x-ray studies show that Dana's  $c$  should be  $c/2$  and that the absolute scale of any cell edge length; e.g.,  $a=7.81\text{\AA}$  at once gives the absolute scale of the oxygen network, placing them at distances  $k/\sqrt{2}=a/2\sqrt{2}=2.76\text{\AA}$  apart on the average.)

Similar treatments of other minerals are given, indicating the scale and orientation of their cubic themes and identifying various X-, U-, V- and W-twins.

<sup>1</sup> Bragg, *Atomic Structure of Minerals*, Cornell University Press, pp. 170–181 (1937).

<sup>2</sup> Dana's *Textbook of Mineralogy*, 3d edition, Wiley & Sons, 1922, pp. 162, 164, 170, 543–544.

## FRACTOGRAPHY

CARL A. ZAPFFE, *Baltimore, Maryland.*

Fractography is the study of the detail seen on nascent cleavage facets at high magnification. Applicable to any substance, crystalline or noncrystalline, this technique leads to observations of special significance because the fracture face, which becomes the plane of observation, is intimately involved with the points and planes of weakness within the structure. In crystalline material, the facet is a crystal face, which offers further advantages and which makes the technique of special interest to crystallographers.

## SOLID PHASE INVERSION IN CALCIUM ORTHOSILICATE

SAMUEL ZERFOSS, *Naval Research Laboratory.*

Calcium orthosilicate shows two types of solid-phase inversions—a sluggish inversion at 675° C. ( $\beta$ — $\gamma$ ) accompanied by a 10% positive volume increase, and a high-low quartz type inversion at 1435° C. ( $\alpha$ — $\beta$ ) of a quite rapid character. The sluggish inversion ( $\beta$ — $\gamma$ ) is inhibited by the introduction of 1% of  $\text{PO}_4$ ,  $\text{BO}_3$ ,  $\text{AsO}_4$ , or  $\text{VO}_4$  ions into the lattice. Work of the writer and recent work of Newman and Wells of the Bureau of Standards showed that these same ions also produce a lowering of the  $\alpha$ — $\beta$  inversion temperature. An attempt is made to explain the inhibition of the sluggish inversion on the basis of our knowledge of the structure of  $\text{Ca}_2\text{SiO}_4$ .

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Dr. James H. C. Martens has resigned his position of Professor of Geology at the University of West Virginia and accepted the appointment of Associate Research Specialist at the Bureau of Mineral Research, Rutgers University, New Brunswick, New Jersey.

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Dr. Terence Thomas Quirke, professor of geology at the University of Illinois, died August 19 of a heart attack at the age of 61 years.

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Dr. Vincent L. Ayres, associate professor of Mineralogy at the Michigan College of Mining and Technology, died at his home in Houghton, Michigan, on October 14, 1947, at the age of 55 years. He had been in ill health for several years and retired from teaching in the spring of 1947.

## BOOK REVIEWS

IGNEOUS MINERALS AND ROCKS by ERNEST E. WAHLSTROM. New York, John Wiley & Sons, 1947. 367 pages, 94 text figures. Price \$5.50.

Professor Wahlstrom's very successful *Optical Crystallography* is now followed by a work on igneous minerals and rocks, designed to serve the requirements of a beginning student in microscopic igneous petrography. Following two chapters on optical and other methods of examining minerals, about a hundred pages are given to the description of the chief families and species that occur in igneous rocks. Here the author has made the wise decision to omit all very rare minerals, as well as doubtful or uncommon varieties. The descriptions are clear, adequate, and well illustrated by photographs and drawings. Next come 42 pages of tables for the identification of minerals, first in thin section and then with immersion media. These tables should be most helpful to students in the laboratory.

The second half of the book deals with igneous rocks. The reviewer wonders why the author did not extend to rocks the same wise discrimination that he applied to the minerals. It is fifty years since James Furman Kemp wrote that:

"one only needs to compile a glossary to appreciate what numbers of unnecessary and ill-advised names for rocks burden this unfortunate branch of science, and to convince one that the philological petrographer comes near to being the enemy of his kind."

The reviewer fondly believed that at the present date the great majority of petrographers were of Kemp's opinion; so it was a blow to find that in this little book Professor Wahlstrom serves up no less than 459 varietal names (not counting compound names), most of which fully merit Kemp's description. What good can it do to a student to learn that "pilandite is a potash trachite" or that "leeuwfonteinite=hatherlite"? Who cares what these obsolete and unnecessary names mean? Scores of other names are equally worthless, but the beginning student has no means of knowing this. Even more discouraging (to the reviewer) than this revival of obsolete rock names is the author's claim that there is no justification for separating rocks containing a little quartz from those that contain a little feldspathoid. Does any chemist hold that there is no justification for separating acid solutions from alkaline solutions? To the reviewer, who has spent much of his petrographic lifetime in trying to persuade his colleagues to abandon the old concept of "rock species" and to look at rocks as chemical systems, Professor Wahlstrom's re-statement of the beliefs of fifty years ago is discouraging.

S. J. SHAND, *Columbia University, New York City*

NOTES ON OPTICAL MINERALOGY by GEORGE TUNELL. California Institute of Technology Bookstore, Pasadena, California, 1946, 39 pages. 15 illustrations. Price \$2.80.

The petrographer seeking a thorough understanding of the elementary principles of optical mineralogy will welcome this collection of notes by a man who has long recognized unsatisfactory definitions of terms and serious inconsistencies and omissions in the treatment of both theory and methods in most American textbooks on the subject. Several comments in this connection are among the author's previous contributions to crystallography. The present notes supply much accurate information—not otherwise readily available—on the behavior of light waves in crystals without rotatory power, and hence they constitute a valuable supplement to textbooks. Owing to their development and publication chiefly for local use, these notes might well escape the attention of some persons interested in the subjects covered; hence a brief review of their contents seems in order.

Included in the text is much material carefully abstracted from the foreign literature,



particularly from Pockels' classic "Lehrbuch der Krystalloptik." The author's own paper on the ray surface, the optical indicatrix, and their interrelation is reproduced in full, with a revised statement on the use of the indicatrix in determining for a biaxial crystal the two wave-normal directions, refractive indices of the two waves, and the vibration directions and velocities of the two rays propagated along any given ray direction. Terms are carefully defined and discussed. For example, uniform usage of the term "vibration direction" in accordance with the electromagnetic theory of light propagation is strongly recommended, and the basic distinction between refractive index and ray index is clearly stated.

Proof of the law of Biot and Fresnel, discussion of Bertin's surface, and treatment of reflection and refraction by means of Huygen's construction and by means of the index surface follow the discussions of the indicatrix and the ray surface. All problems are solved by simple geometrical means, rather than in basic terms of mathematical equations. Advantages and limitations of methods are pointed out.

Collated data on six reference surfaces of optically biaxial crystals are presented in a simple tabular form that should greatly facilitate understanding of their respective characteristics. The reviewer knows of no such compilation in the English literature. A closing section entitled Optical Crystallography comprises a glossary of important terms; an outline of properties to measure and features to look for under the petrographic microscope; a table of crystal systems, crystal classes (point groups), optical classes, types of dispersion, and presence or absence of rotatory power; and a selected and partly annotated bibliography.

The petrographer will find these notes of considerable reference value for the theories underlying the rule-of-thumb methods commonly used in the laboratory, and the interested student of optical crystallography will find them a well-documented introduction to more advanced problems of light transmission through crystals.

RICHARD H. JAHNS,  
*California Institute of Technology,  
Pasadena, California*

**HANDBOOK OF URANIUM MINERALS** by JACK DEMENT AND H. C. DAKE. Mineralogical Publishing Company, 329 S.E. 32nd Avenue, Portland 15, Oregon; 1947, 80 pages, price \$1.50.

This booklet is an interesting, elementary compilation of data relating to the uranium and thorium minerals. It is written in a popular style and should prove of much interest to collectors, prospectors, and those desiring a handy, general introduction to the subject.

A chapter on the occurrence of uranium minerals gives a survey of their distribution throughout the world. It is somewhat uneven in its treatment of the occurrences in the various states and there are some omissions. For example, no mention is made in this chapter of the occurrence of carnotite at Mauch Chunk, Pennsylvania, nor of the occurrence of any uranium or thorium minerals in occupied Germany.

A chapter on the prospecting for and detection of uranium minerals presents a general discussion of the various methods. The description of the use of the Geiger-Müller counter by G. C. Ridland in the geologic survey of the pitchblende veins at Great Bear Lake, Canada, will be of particular interest.

Two chapters are devoted to the uranium and thorium minerals. Carnotite and pitchblende are treated in some detail in the first chapter. The second chapter gives brief data on each mineral. Comparison of the data on minerals, spelling of names, and synonymy, in this booklet with those in Volume 1 of *Dana's System of Mineralogy*, seventh edition, shows that the writers did not make full use of the treatment by Palache, Berman, and

Fron del. The description of the uranium and thorium minerals is not complete and it is surprising that allanite, gadolinite, and zircon are not mentioned as uranium or thorium bearing minerals.

The book is concluded with a selected bibliography, a reference to original papers on radioactive minerals, and five short appendices on radiochemical data.

The book appears to have been hastily compiled, as is indicated by the frequent misspellings and inconsistencies in the text.

GEORGE T. FAUST

**THE MINERAL KEY** by HOWARD B. GRAVES, JR. (Chemist, Research Division, International Minerals and Chemical Corporation; formerly Chemist, E. I. DuPont de Nemours; formerly Geologist, The Texas Company). 178 pages,  $4\frac{1}{2} \times 7$ . McGraw-Hill Book Co., Inc., 1947. Price \$4.00.

This book is designed especially for amateur mineralogists and mineral collectors. About 125 of the 178 pages are devoted to determinative tables listing 823 minerals. These tables are based on the usual physical properties (specific gravity not included), with supplementary chemical tests to confirm identification.

Keeping in mind that the reader is quite likely to have had no specialized training in mineralogy, the author has omitted a discussion of crystallography and has restricted his tests to those that involve only the common chemicals and the simpler apparatus. (Useful tests not listed include the Cassius purple test for gold; the dimethylglyoxime test for nickel; the ammonium molybdate test for phosphorus; also no tests for beryllium, cerium or platinum.)

Additional tables are given for minerals with fibrous and earthy textures and for members of the mica family (micas, chlorites and vermiculite).

The Mineral Key should prove helpful to prospectors, mining engineers and geologists located in places where laboratory facilities are very limited, but the high price of \$4.00 seems excessive for so small a book without a single cut or illustration.

W.F.H.

*University of Michigan*

**THE DEVELOPMENT OF THE CHEMICAL ELEMENTS** by N. EFREMOV.

*The Development of the Chemical Elements* is an 80-page treatise, in German translated from Ukrainian, by Dr. N. Efremov, Professor of Mineralogy and Petrography at the International UNRRA University in Munich, Germany. The paper-covered volume, which was published in 1946 under the authority of UNRRA Team 108 by Ludwig Storr, 5 Liebherr Street, Munich, embodies Dr. Efremov's ideas on the nature of geochemical changes and reactions. In the introduction the author draws an analogy between the man-made explosions at Hiroshima and Bikini and such "geological explosions" as the eruptions of Mont Pelée and Krakatau, and presents the hypothesis that the ultimate source of energy for the two is the same. In brief, the hypothesis, which he calls atomic heteromorphosis, states that transformation of elements (other than radioactivity) takes place within the earth and that this transmutation of atoms furnishes energy for many earth processes and is the basis for numerous petrological and mineralogical reactions.

The transformation reactions are divided into two types: (1) those which proceed without the introduction of other elements such as  $Mg + Mg = Na + Al + \text{free energy}$ , and (2) those which proceed with the addition of other elements as typified by  $He + Ca = Al + OH$ . Using these two types of reactions the author proceeds to write numerous mineralogical equations to embellish his ideas on petrogenesis. He advances the concept of

a primary dunitic magma from which many types of igneous rocks could be derived by elemental transformation. Olivine, which he regards as the original mineral, can be converted, through changes in the magnesium molecule, into any of the following: anorthite, albite, corundum, pyrope, enstatite, serpentine, spinel, nepheline, or orthoclase. Thus from dunite are derivable peridotite, pyroxenite, picrite, gabbro, basalt, diabase, serpentine, albitite, essexite-basalt, atlantite, theralite, and nepheline syenite, among others.

The problems of serpentinization and the origin of feldspathoidal rocks are also examined from the viewpoint of the new hypothesis. The author rejects the idea that serpentine results from the action of water on olivine-rich rocks and substitutes the transformation reaction:  $Mg = 4H + O + \text{energy}$ . The source of the feldspathoidal magma lies in the transformation previously cited, that of two molecules of magnesium into one of sodium and one of aluminum, by means of which olivine is changed to nepheline. According to the author this transformation "plays an unusually important role with respect to Ca and Mg in the life of the planet, for it postulates the origin of the alkalic aluminosilicate magmas."

Professor Efremov has presented some highly original thoughts on various petrological problems, and his hypothesis makes interesting reading. His enthusiasm for his brainchild is boundless, as witnessed by the following statement made in rejecting Bowen's theory of crystal differentiation: "These inadequacies (of Bowen's theory) are lacking in the hypothesis of heteromorphism, for it devises an interpretation for all our known petrological and geological phenomena with striking simplicity and elegance." The chief weakness of the concept seems to lie in the assumption that atomic transmutation, other than radioactivity, is of a common and widespread occurrence within the earth. Under laboratory conditions enormous quantities of energy are required for elemental transformation, yet the author fails even to speculate regarding possible conditions for this phenomenon on a geological scale. The organizational pattern of the treatise is somewhat haphazard and increases the difficulty of following the sometimes abstruse argumentation. Most of the illustrations are only remotely concerned with the ideas advanced in the text.

E. WM. HEINRICH  
*University of Michigan*

## NEW MINERAL NAMES

### Apoanalcite

CHRISTOFFER OFTEDAHL, Apoanalcite, a new mineral. *Norsk Geol. Tidsskrift*, **26**, 215-218 (1947).

PHYSICAL PROPERTIES: Red, massive, slightly columnar. Optically positive, uniaxial,  $n_E = 1.487$ ,  $n_O = 1.475$ .

CHEMICAL PROPERTIES: Analysis by Lars Lund (on 0.2 g. for the main portion and on 0.13 g. for alkalis):  $SiO_2$  41.2,  $Al_2O_3$  34.0,  $CaO$  0.7.,  $Na_2O$  12.2,  $K_2O$  tr.,  $H_2O$  11.7; sum 99.8%. This gives  $Na_{0.92}Ca_{0.03}Al_{1.65}Si_{1.59}O_6 \cdot 1.51 H_2O$ . The mineral therefore does not correspond to the normal zeolite type, in which each Al replacing Si is balanced by one Na. Dehydration study by Lars Lund gave a curve with a sharp break, 1.01% being lost at 300°, 9.40% at 420°.

OCCURRENCE: In an erratic boulder of syenite pegmatite in a gravel pit at Voksen, 5 km. N. W. of Oslo. The specimen contains chiefly gray micro-perthite with some aegirine and biotite crystals. It is suggested that some of the massive red "natrolite" of this area may prove to be apoanalcite.

DISCUSSION: The composition and the birefringence are distinct from those of normal analcime, but further study, especially x-ray, is needed.

MICHAEL FLEISCHER

**Mavinite**

B. RAMA RAO, "Kyanophilitite"—a new mineral of the hydrous aluminum silicate group, and "mavinite"—a new type of brittle mica, from Mavinhalli, Mysore. *Records Mysore Geol. Dept.*, **43**, 17–30 (1944) (Publ. 1946).

PHYSICAL PROPERTIES: Monoclinic, tabular or platy aggregates forming small books like micas. Often twinned. Cleavage basal, less perfect than in micas. Laminae slightly flexible, but inelastic and brittle. Sectile.  $H=2-2\frac{1}{2}$ ,  $G=2.90$ . Color dark bottle-green in thick sheets, very pale green in thin laminae.

Optically biaxial positive,  $2V$  about  $30^\circ$ , mean  $n=1.626\pm.001$ , birefringence very low,  $\gamma-\alpha$  approx. 0.004. Pleochroism very faint,  $X$  almost colorless to very pale bluish-green,  $Z$  very pale yellowish-green.

CHEMICAL PROPERTIES: Analysis by E. R. Tirumalachar of material free from inclusions, dried at  $105^\circ$ , gave  $SiO_2$  30.33;  $Al_2O_3$  45.67;  $Fe_2O_3$  1.58;  $FeO$  2.96;  $MgO$  7.24;  $CaO$  none;  $MnO$  none; alk. tr.; loss on ignition 12.52; sum 100.30%. Apparently a member of the chlorite group.

OCCURRENCE: Occurs near Mavinhalli, Mysore, India, as loose bits at the contact of enstatite peridotite with graphite-kyanite schists and sillimanite-biotite gneisses. Not found in place in fresh rocks. It is believed to be formed by contact metamorphism resulting from the intrusion of peridotite into pre-existing altered aluminous rocks.

NAME: For the locality.

M.F.

**NEW DATA****Kyanophilitite**

B. RAMA RAO, "Kyanophilitite"—a new mineral of the hydrous aluminum silicate group, and "mavinite"—a new type of brittle mica, from Mavinhalli, Mysore. *Records Mysore Geol. Dept.*, **43**, 17–30 (1944) (Publ. 1946).

An abstract of a preliminary report on this mineral has been printed in *Am. Mineral.*, **32**, 255 (1947). Additional data are now presented. Two analyses by E. R. Tirumalachar on material dried at  $110^\circ$  gave  $SiO_2$  46.98, 46.60;  $Al_2O_3$  38.09, 38.57;  $Fe_2O_3$  1.13, 0.71;  $MgO$  0.85, 0.75;  $CaO$  none, none;  $Na_2O$  2.09, 1.54;  $K_2O$  5.46, 7.81; loss on ignition 5.40, 5.00; sum 100.00, 100.98%. The analysis previously printed of a third sample differs from these in showing sodium predominant over potassium. Optically biaxial, negative (?). Indices of refraction  $\alpha=1.577$ ,  $\beta=1.580$ ,  $\gamma=1.584$ , all  $\pm.002$ .  $G=2.89-2.90$ ,  $H=4$  on fresh faces,  $2\frac{1}{2}-3$  on exposed faces. No cleavage observed, fracture uneven and splintery.

DISCUSSION: Perhaps members of the ill-defined hydrous mica group. Evidently not a single mineral, since both sodium-bearing (rectorite?) and potassium-bearing (bravaisite, illite?) varieties are included.

M.F.

**Dunhamite**

The new mineral name dunhamite was proposed in a paper by E. E. Fairbanks published in *Econ. Geol.*, **41**, 761–768 (1946). I commented (*Am. Mineral.*, **32**, 372 (1947)), "It is not clear whether Fairbanks re-examined this material or depended on the literature entirely." Mr. Fairbanks has now informed me that the optical data and etch tests he recorded in his paper were his own observations, made on 50 polished sections. Furthermore, he made contact print tests that showed Pb and Te to be the principal constituents of the mineral, as had previously been conjectured, but not proved.

M. F.



## DISCREDITED MINERALS

**Minervite and Palmerite (=Taranakite)**

F. A. BANNISTER AND G. E. HUTCHINSON, The identity of minervite and palmerite with taranakite. *Mineralog. Mag.*, **28**, 31-35 (1947).

X-ray, optical, and specific gravity determinations were made on taranakite (Hector and Skey, 1865) from the Sugarloaves, Taranaki, New Zealand, palmerite (Casoria, 1904) from Monte Alburno, Italy, and minervite (Carnot, 1895) from Minerva grotto, Hérault, France. These three hydrous potassium aluminum phosphates gave identical x-ray powder photographs, had *ns*, respectively, 1.502, 1.507, and 1.50; *G.*, respectively, 2.15, 2.15, not detd. The published analyses differ considerably; the composition is arbitrarily taken as  $K_2O \cdot 3(Al, Fe)_2O_3 \cdot 3P_2O_5 \cdot 18H_2O$ , from Casoria's analysis. The name taranakite has priority.

M.F.

**Richmondite**

C. OSBORNE HUTTON, Richmondite, a discredited mineral. *Nature*, **159**, 817 (1947).

Richmondite was described in 1877 by Skey as a lead, copper, iron, antimony sulfide, with minor silver and zinc, from Richmond Hill, New Zealand (See *Dana's System*, 7th edition, volume 1, page 393). Hutton has examined polished surfaces "from a number of specimens labelled 'Richmondite' that exhibit the properties described by Skey." He finds them to be mixtures containing, in order of abundance, argentian tetrahedrite, galena, sphalerite, chalcopyrite, pyrite, and perhaps stromeyerite.

DISCUSSION: Presumably the material examined was from the type locality, but this is not explicitly stated.

M.F.

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